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Carbon Stabilised Saponite Supported Transition Metal-Alloy Catalysts for Chemical CO₂ Utilisation via Reverse Water-Gas Shift Reaction

N. Nityashree†,1, C. A. H. Price†,2, L. Pastor-Perez2, G. V. Manohara1, S. Garcia1, M. M. Maroto-Valer1, *, T. R. Reina2, *

† These authors share equal contribution to this work.

Research Centre for Carbon Solutions (RCCS), School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, United Kingdom.

Department of Chemical and Process Engineering, University of Surrey, Guildford, GU2 7XH, United Kingdom.

Corresponding author/s: m.maroto-valer@hw.ac.uk (M. M. Maroto-Valer) and t.ramirezreina@surrey.ac.uk (T. R. Reina)

Graphical Abstract
Highlights:

- Economically viable catalysts for gas phase CO$_2$ upgrading
- Ni promoted active phases supported on saponite clay as *nature inspired* catalysts
- Advantageous bimetallic Ni-Cu formulation to suppress methanation.
- Remarkable selectivity for low temperature RWGS using Ni-Cu/Saponite

Abstract: Chemical CO$_2$ upgrading via reverse water gas shift (RWGS) represents an interesting route for gas phase CO$_2$ conversion. Herein, nature inspired clay-based catalysts are used to design highly effective materials, which could make this route viable for practical applications. Ni and transition metal promoted Ni saponite clays has been developed as highly effective catalysts for the RWGS. Saponite supported NiCu catalyst displayed a remarkable preference for the formation of CO over CH$_4$ across the entire temperature range compared to the saponite supported NiCo and Ni catalysts. The NiCu sample is also highly stable maintaining ~ 55% CO$_2$ conversion and ~ 80% selectivity for CO for long terms runs. Very importantly, when compared with reference catalysts our materials display significantly higher levels of CO$_2$ conversion and CO selectivity. This confirmed the suitability of these catalysts to upgrade CO$_2$-rich streams under continuous operation conditions.

Keywords: CO$_2$ conversion, Saponite, supported metal alloy catalysts, reverse water gas shift reaction, CO selectivity.

1. Introduction

Extensive use of fossil fuels is largely contributing to CO$_2$ emissions and global warming. The current efforts of the scientific community is to develop sustainable technologies that can reduce CO$_2$ emissions or even reach net zero or negative emission through the capture and conversion of CO$_2$ [1]. CO$_2$ conversion into CO, CH$_4$, cyclic carbenes, polymers, etc can be achieved by a variety of methods [2-6]. CO$_2$ capture and utilisation to produce fine chemicals accounts for a small percentage of the emitted CO$_2$ levels [7]. A possible way to reach net zero emissions of CO$_2$ is to use fuels that are derived from emitted CO$_2$ [8, 9]. However, CO$_2$ is a stable molecule that requires a great deal of energy to activate, and therefore, efficient and low-
cost conversion methods and catalysts for CO₂ activation and conversion are highly sought. Current research in this area concern the use of Cr, Fe, Ni and Cu doped with a variety of materials (i.e. Ce, Cs, Zr or Y) or using photocatalysts in a photo-assisted reverse water gas shift. Although the active phase varies quite considerably among these materials, the support media largely remains the same, usually metallic oxides like Al₂O₃, CeO₂, ZrO₂ or doped/mixed combinations.

Production of higher hydrocarbon fuels through processes like the Fischer-Tropsch (F-T) synthesis and hydrogenation of CO₂ to form methanol via reverse-water-gas-shift reaction (CAMERE process) are promising routes to utilise emitted CO₂ [10, 11]. F-T synthesis and CAMERE processes reported better efficiencies (approximately 20%) when CO generated from RWGS reaction was used as raw material [11]. Conversion of CO₂ to CO through RWGS reaction is shown in (eq. 1). The reaction is endothermic and as such, is expected to demonstrate increased efficiencies at higher temperatures. There exists a major competing exothermic methanation reaction (Sabatier process), (eq. 2) that occurs at lower temperatures producing methane. A highly unwanted material where F-T or CAMERE processes are concerned.

\[
\begin{align*}
\text{CO}_2 + \text{H}_2 & \leftrightarrow \text{CO} + \text{H}_2\text{O}; \Delta H_{298} = +41 \text{ kJ/mol} \quad (1) \\
\text{CO}_2 + 4\text{H}_2 & \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}; \Delta H_{298} = -165 \text{ kJ/mol} \quad (2)
\end{align*}
\]

As an additional drawback, the Sabatier reaction consumes 4 moles of hydrogen per mol of CO₂ thus imposing extra process cost. In this regard, if we aim to design an efficient reverse water gas shift unit, it is of paramount importance to control the competition CO₂-Methanation/RWGS to ensure the process is selective towards carbon monoxide. In this sense, a variety of catalytic materials has been investigated for RWGS reaction [12-15]. Noble metals, such as Au, Pt, Pd, Rh and Ru, exhibit high activity, stability and selectivity for CO₂ reduction to CO. However, due to their cost and scarcity, it is desirable to replace these materials by introducing more economically appealing catalysts. Transition metals-based catalysts represent an economically interesting alternative [16]. For instance, copper-based catalysts were found to be more selective for CO production favouring RWGS reaction [17-24]. However, they suffered stability problems [25]. Modified Ni-based catalysts were also designed to achieve better selectivity and stability for RWGS reaction [26]. Bimetallic or metal alloy catalysts of Cu, Ni and Co exhibited activities comparable to noble metals and their alloys but, had stability issues [27]. Hence, in addition to catalyst activity and selectivity
for CO, stability and sustainability of the chosen catalyst at reaction conditions are also critical.

The nature of the catalyst support is known to influence the coking characteristics, stability and dispersion of catalysts. Different supports interact differently with the active catalyst [28, 29]. For example, CeO₂ supported Au was more active than the TiO₂ supported Au catalyst due to the higher oxygen mobility of CeO₂ [30]. *In situ* generated carbon support due to decomposition of a metal organic framework precursor showed high stability of the catalyst [31]. Mixed oxide supports of CeO₂/ZrO₂ or CeO₂/Al₂O₃ supporting Ni altered the activity and selectivity of the catalyst when compared to unsupported Ni [26, 32]. Reduced surface acidity of Al₂O₃ modified with CeO₂ caused lesser extent of coking and retained catalyst activity for a longer time [33]. Specialised methods such as magnetron sputtering, atomic layer epitaxy (ALE), atomic layer/chemical vapour deposition, etc have also been employed to increase catalyst activity and stability [34, 35]. Avoiding sophisticated, expensive techniques and excessive use of chemicals in catalyst preparation would make the whole process commercially more viable.

Accordingly, it would be advantageous to design a sustainable synthesis of transition metal-based catalysts supported on low-cost, environmentally benign supports such as clays. Saponite is a smectite clay, having the formula NaMg₆(Si₇Al)O₂₀(OH)₄, with magnesium substituted 2:1 aluminosilicate layers and interlayer regions occupied by Na⁺ ions and water molecules. A number of transition metal based saponite catalysts has been used as catalysts in reducing gaseous compounds [36]. Change in the surface acidity of the magnesio-aluminosilicate clay layers in comparison to Al₂O₃ could affect the overall catalyst dispersion and stability. Recently, adamantane carboxylates of transition metals and alkaline earth metals have been synthesized by sustainable green protocols. These adamantane carboxylates under controlled decomposition are known to generate *in situ* carbon that stabilize metal nanoparticles/metal oxides/mixed metal oxides [37].

In this paper, aqueously exfoliated saponite clay layers have been used to provide better dispersibility and higher thermal stability to the active catalyst. The catalyst precursors, saponite-transition metal adamantanecarboxylates have been prepared by using metal hydroxides and 1-adamantane carboxylic acid. The resultant saponite / transition metal adamantanecarboxylates were reduced under hydrogen to achieve saponite supported carbon stabilized NiCu and NiCo metal alloy nanoparticles – our *nature inspired*
multicomponent catalysts. These catalysts were then tested for reduction of CO₂ to CO through RWGS reaction. The selectivity, activity and long-term stability of the resultant catalysts were tested and compared with that of monometallic Ni catalyst supported on saponite.

2. Experimental

2.1. Synthesis of Catalyst

Ni(OH)₂, Cu(OH)₂ and Co(OH)₂ were used as the transition metal sources, and 1-adamantanecarboxylic acid, used as the carboxylate source (All chemicals were procured from Sigma Aldrich and used as received without further purification). Deionised water (18 MΩ.cm resistivity, Millipore water purification system) was used throughout the experiment. Na⁺-saponite, Na₆Mg₆(Si₇Al)O₂₀(OH)₄, was synthesized hydrothermally by a procedure reported by Kawi and Yao [38].

In a typical synthesis of saponite supported NiCu-adamantanecarboxylate (NiCu-Ada/Sap), 1 g of Na⁺-saponite was stirred in 100 ml of water for 2 days at room temperature to produce exfoliated colloidal dispersion of saponite clay. 3.79 g 1-adamantanecarboxylic acid and 0.5 g Ni(OH)₂ and 0.5 g Cu(OH)₂, (1-adamantanecarboxylic acid / M = 2) were added to the 100 ml exfoliated saponite suspension and stirred for 1 hour at room temperature. This reaction mixture was then transferred into a teflon-lined vessel and hydrothermally treated at 150 °C for 24 h. The resultant product was washed with excess of water to remove any ionic impurities and dried at 75 °C overnight. The preparation of saponite supported NiCo-adamantanecarboxylates (NiCo-Ada/Sap) and Ni-adamantanecarboxylates (Ni-Ada/Sap) followed the same procedure, except that 0.5 g of Co (OH)₂ was used instead of Cu (OH)₂ and 3.88 g 1-adamantanecarboxylic acid was used for synthesis of NiCo-Ada/Sap. Ni-Ada/Sap was synthesised by using 0.5 g Ni (OH)₂ with 1.75 g of 1-adamantanecarboxylic acid by following the same procedure.

Saponite supported metal/metal alloys were synthesized by decomposing the catalyst precursors, NiCu-Ada/Sap, NiCo-Ada/Sap and Ni-Ada/Sap under reducing atmosphere by passing H₂. In a typical decomposition experiment, about 1.0 g of the catalyst precursors was loaded into a quartz tube and subjected to decomposition at 600 °C under H₂ atmosphere (50 ml/min, 10 °C/min, residence time 2 h).
2.2. Catalyst Characterization

Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance power diffractometer, using Ge-monochromated Cu-K\(\alpha\) radiation (\(\lambda = 1.5406\) Å) from a sealed tube, operating at 40 kV and 40 mA with a Lynx Eye linear detector in reflectance mode. Data were collected over 2\(\theta\) angular range of 2-90° with a step size of 0.009°. Fourier Transform Infrared spectra (FTIR) of samples were measured using Perkin Elmer spectrometer in ATR mode (4000-600 cm\(^{-1}\)). Thermal analysis of the precursor samples was performed using a thermogravimetric analyser (TA Instruments TA 500). C and H analysis of the precursor samples was carried out by placing approximately 3 mg of sample in a tin capsule and combusting in a high oxygen environment at 950°C using an Exeter Analytical CE-440 elemental analyser calibrated with acetonilide. Metal loading on saponite in NiCuSap, NiCoSap and NiSap were quantified by XRF using a Panalytical Zeitium WD-XRF with a 4kW rhodium anode tube in helium path. During XRF analysis, each sample was weighed accurately and placed in the sample cups under helium path. The cups were prepared with 50-micron prolene film.

Raman spectra were recorded using Renishawin Raman Microscope with a 785 nm red laser operating WiRE® version 4.2. The data was obtained using a 10s exposure time with 5 – 10% laser power.

X-ray Photoelectron Spectroscopy (XPS) was undertaken using a K-ALPHA Thermo Scientific device, utilising Al-K radiation (1486.6 eV) and a twin crystal monochromator to produce a focussed x-ray spot at 3 mA x 12 kV (400 \(\mu\)m major axis length of the elliptical shape). Prior to the spectral acquisition, the samples were pre-reduced simulation the activation treatment. The data was then processed using the Avantage software package.

\(\text{N}_2\) adsorption isotherms and textural analysis was performed on a Micrometrics 3Flex at 77 K over P/P\(_0\) 0-0.99 under nitrogen. Transmission electron microscopy (TEM), high resolution TEM (HRTEM) images are acquired using a FEI Titan Themis instrument equipped with a FEI SuperX EDX detector. Surface morphology and elemental analysis of spent catalyst were done by using JEOL 7100F scanning electron microscope (SEM) microscope with an Energy Dispersive X-Ray spectrocope (EDX) to determine both active phase dispersion and the presence and type of coking. Oxidation TGA experiments were undertaken on a Q500 V6.7, ramping from room temperature to 900 °C at 10 °C/min in air. Cation exchange capacity (CEC) was estimated by a method reported by Chapman et al. [39] by
exchanging Na⁺ ions in Na⁺-saponite with NH⁴⁺ ions for three consecutive times with 1N NH₄CH₃COO solution. 0.1 g of saponite was stirred with 10 mL of NH₄CH₃COO solution for 30 minutes. The supernatant was separated from saponite and collected in a volumetric flask. The exchange reaction with NH₄CH₃COO solution was repeated two more times and the supernatant collected as before into the same volumetric flask. The supernatant was diluted suitably to estimate for Na⁺ ions by comparing with a set of standard solutions using iCE 3300 AA Thermo Fischer Scientific Atomic Absorption Spectrophotometer (AAS). Na⁺ ions were estimated using Na- hollow cathode lamps at 589 nm under air/acetylene flame.

2.3. Catalytic Activity Studies

The RWGS experiments were conducted in a tubular quartz reactor (10 mm ID) at atmospheric pressure. The catalysts were supported on a layer of quartz wool acting as a bed. The reactant gas flow used for temperature screening and stability tests contained CO₂ and H₂ in a ratio of 1:4 balanced with N₂ to maintain a WHSV = 15 L/g_cat h. The gas products were analysed using an online gas analyser (ABB AO2020, ABB Ltd., Zurich, Switzerland) equipped with both an IR and TCD detectors. All catalysts were reduced pre-reaction in the reactor by flowing 100 mL min⁻¹, 20% H₂/ 80% N₂ at 850°C for 1 hour. Temperature screening reactions were conducted using a temperature range of 300–850 °C at 50 °C intervals. The stability study was conducted at 500 °C for 89 hours.

3. Results and Discussion:

3.1. Catalyst Characterization

Saponite supported metal-adamantanecarboxylates were prepared by hydrothermally treating the respective metal hydroxides with twice the number of moles of 1-adamantanecarboxylic acid in the presence of exfoliated saponite clay layers as described in the experimental section. Only the required stiochiometric amounts of metal hydroxides (metal ion source) and 1-adamantanecarboxylic acid (carboxylate ion source) were used for the synthesis and no excess amounts of chemicals were used. Exfoliation of smectite clays in water is spontaneous and well known [40]. Exfoliated clay layers have been used as 2D starting materials for synthesis of various composites [41]. Using exfoliated clay layers as opposed to bulk clays enables homogeneous mixing in the catalyst precursors by accessing the interlayer regions that were generally inaccessible prior to exfoliation. Metal hydroxides and 1-adamantanecarboxylic acid under hydrothermal conditions were precipitated as
NiCu/NiCo/Ni-adamantanecarboxylates over the clay sheets. 1:2 ratio of metal to 1-adamantanecarboxylic acid was taken as divalent metal cations would need two monovalent 1-adamantanecarboxylate ions for charge compensation. The elemental (C and H) analysis of the resultant catalyst precursors (table S1, supporting information) confirms the presence of expected amounts of 1-adamantanecaboxylates in the samples. Excess amount of hydrogen was observed due to OH groups of clay layers and adsorbed water molecules.

PXRD patterns of the as synthesized catalyst precursors and pristine saponite are shown in Fig. 1 (a-d). Saponite (Fig. 1a) shows first basal (00l) reflection at d-spacing of 12.56 Å that matches well with the values reported for sodium ion intercalated saponite [38]. Other reflections observed at higher 20 values of about 19.6°, 28.7°, 35.5° and 60.5° correspond to the 2D reflections of saponite. The (060) reflection at 60.55° with d-value of 1.53 Å categorises saponite as a tri-octahedral smectite clay [38]. Empirical formula for saponite deduced from XRF analysis was found to be Na0.97Mg5.96Si6.94Al0.93O24.20H5.38. CEC of saponite that evaluates the amount of exchangeable interlayer cations in the clay was estimated by a method reported by Chapman et al. [39]. CEC of Na+-saponite was found to be 123 meq/100 g which is quite high for smectite clays. High CEC values indicates spontaneous swelling and exfoliation of clays in water [42]. High degrees of exfoliation results in homogeneous composite precursors as the exfoliated 2D alumino-silicate clay layers are available for composite formation. Surface properties such as surface area, pore size and pore volume of the saponite was calculated by N2 adsorption technique as described in the experimental section. The saponite clay shows BET surface area of 147 m2/g and pore diameter and volume were 3.1 nm and 0.118 cm3/g respectively. Surface area value of saponite indicate a well stacked clay layers formed due to hydrothermal method of synthesis followed as reported [43]. The PXRD patterns of Ni-Ada/Sap, NiCo-Ada/Sap and NiCu-Ada/Sap catalyst precursors shown in Fig. 1b, c and d respectively match well with Ni, Cu and Co-metal adamantane-carboxylates reported in literature [37]. Ni-Ada/Sap (Fig. 1b) shows characteristic reflections at 20 values 6.09°, 6.29°, 6.76°, 11.10°, 12.03°, 15.97°, 16.57°, 17.77° and 24.25° corresponding to d-values of 14.49 Å, 14.03 Å, 13.06 Å, 7.96 Å, 7.35 Å, 5.54 Å, 5.35 Å, 4.98 Å and 3.66 Å respectively. Similar reflections were seen in the PXRD pattern of NiCo-Ada/Sap in Fig. 1c. PXRD pattern of NiCu-Ada/Sap catalyst precursor (Fig. 1d) have additional reflections (at 20 values of 7.49° and 8.69° corresponding to d-values of 11.78 Å and 10.16 Å respectively) compared to the other catalyst precursors and this observation matches well with previous reports [37]. The (00l) reflection of saponite is not
observed in the catalyst precursors, due to higher intensity of the metal adamantanecarboxylates phases. However, the 2D reflections of saponite clay layers are observed in the enlarged portion of the PXRD patterns of the catalyst precursors [Fig. S1 (supporting information)]. PXRD patterns of all the catalyst precursors, thereby, indicate composite formation of metal adamantanecarboxylates with saponite.

![Figure 1. PXRD patterns of (a) pristine saponite, (b) Ni-Ada/Sap, (c) NiCo-Ada/Sap and (d) NiCu-Ada/Sap.](image)

Figure 1. PXRD patterns of (a) pristine saponite, (b) Ni-Ada/Sap, (c) NiCo-Ada/Sap and (d) NiCu-Ada/Sap.
Figure 2. FTIR spectra of (a) pristine saponite, (b) Ni-Ada/Sap, (c) NiCo-Ada/Sap and (d) NiCu-Ada/Sap.

FTIR spectra of all the catalyst precursors (Fig. 2b-d) and saponite (Fig. 2a) show a characteristic strong Si-O stretching vibration at around 950 cm\(^{-1}\). Similarly, the hydrogen bonded O-H stretching vibration is observed in all the samples at ca. 3400 cm\(^{-1}\). All - trans, C-H stretching modes are observed at 2850 cm\(^{-1}\) and 2900 cm\(^{-1}\) in the catalyst precursors (Fig. 2b-d), attributed to the adamantane moiety. COO\(^{-}\) stretching vibrations (Fig. 2b-d) observed between 1350 cm\(^{-1}\) and 1550 cm\(^{-1}\) confirm the presence of carboxylate ions in the catalyst precursors. The absence of C-H and the carboxylate vibrations in Na\(^{+}\)-saponite is evident from Fig. 2a. PXRD and FTIR analysis of the resultant precursor catalysts show the successful composite synthesis of metal adamantanecarboxylates over saponite clays sheets, as anticipated.
Figure 3. Thermogravimetric analysis of (a) pristine saponite, (b) Ni-Ada/Sap, (c) NiCo-Ada/Sap and (d) NiCu-Ada/Sap.

Fig. 3 shows the thermal decomposition profile of Ni-Ada/Sap (Fig. 3b), NiCo-Ada/Sap (Fig. 3c) and NiCu-Ada/Sap (Fig. 3d) and saponite (Fig. 3a) under nitrogen gas flow as described in the experimental section. The different thermal decomposition profiles of the catalyst precursors in comparison to pristine saponite clay further indicates their composite nature. The NiCo-Ada/Sap and NiCu-Ada/Sap loses mass in three steps leaving about 30 wt% residues. Ni-Ada/Sap loses 50 wt% of mass, whereas saponite loses about 15 wt% of its mass in accordance to previous reports [38]. Lower mass loss in the case of Ni-Ada/Sap in comparison to NiCo-Ada/Sap and NiCu-Ada/Sap samples was expected due to lower amounts of metal-adamantanecarboxylate in Ni-Ada/Sap. DTG profiles of the catalyst precursors are given as supplementary information, Fig. S2. All samples show a mass loss below 200 °C that could be due to loss of water molecules. Pristine saponite sample (Fig. S2a) loses mass in two more steps at 557 °C and 749 °C due to loss of water of hydration, dehydroxylation of outer and inner hydroxyl ions as reported in literature [41]. Mass loss of Ni-Ada/Sap (Fig. S2b), NiCo-Ada/Sap (Fig. S2c) and NiCu-Ada/Sap (Fig. S2d) in between 200 – 550 °C could be due to the degradation of the metal-adamantanecarboxylates in the catalyst precursors.
The catalyst precursors, NiCu-Ada/Sap, NiCo-Ada/Sap and Ni-Ada/Sap were reduced under hydrogen, as described in the experimental section, to obtain saponite supported NiCu, NiCo and Ni metal alloys/metal nanoparticles. PXRD patterns of the freshly prepared active catalysts NiSap, NiCuSap and NiCoSap are shown in Fig. 4a, b and c respectively. Reflections due to the Ni metal, NiCo and NiCu alloys were observed along with those due to saponite. The reflections of Ni-metal (Fig. 4a) appear at 2θ values of 44.42°, 51.84° and 76.33° with d-values of 2.04 Å, 1.76 Å and 1.25 Å, respectively. Similarly, reflections due to NiCu-alloy (Fig. 4b) are seen at 2θ values of 43.99°, 51.26° and 75.32° with d-values of 2.06 Å, 1.78 Å and 1.26 Å respectively. While, reflections due to NiCo-alloy (Fig. 4c) are seen at 2θ values of 44.37°, 51.63° and 76.06° with d-values of 2.03 Å, 1.76 Å and 1.49 Å, respectively. Reflections due to saponite in the freshly prepared catalysts were observed at 19.67°, 28.42°, 31.12° and 35.99°. The resultant active catalyst was also characterised using

Figure 4. PXRD patterns of (a) NiSap, (b) NiCuSap and (c) NiCoSap.
FTIR as shown in supporting information, Fig. S3. All samples show vibrations due to Si-O at 950 cm\(^{-1}\) due to saponite and C=C vibration (1600 cm\(^{-1}\)) due to residual carbon. The samples also show a broad vibration at 3400 cm\(^{-1}\) due to adsorbed water.

The metal loadings on saponite were determined by XRF analysis. Table 1 shows the amount of Cu, Co and Ni present in various samples per gram of catalyst. The resultant catalysts were further characterized with Raman spectroscopy (Fig. S4, supporting information). The Raman spectra of the freshly prepared catalysts showed two intense bands which are attributed to vibration modes of sp\(^2\)-bonded carbon atoms. The G-band observed at 1594 cm\(^{-1}\) is due to the sp\(^2\) carbon stretching modes in aromatic rings derived from the incomplete decomposition of 1-adamanatane-carboxylate unit. The peak at approx. 1336 cm\(^{-1}\) is the graphitic D-band that becomes active in the presence of structural disorders [44].

| Sample   | Elemental Percentage Composition (g\(_{\text{cat}}^{-1}\)) | Ni (wt %) | Cu (wt %) | Co (wt %) |
|----------|-------------------------------------------------------|-----------|-----------|-----------|
| NiCuSap  | 13.91                                                 | 13.50     | -         | -         |
| NiCoSap  | 14.92                                                 | -         | 15.11     | -         |
| NiSap    | 14.79                                                 | -         | -         | -         |

The role played by the solid surface is essential in catalysis. Herein, x-ray photoelectron spectroscopy (XPS) allows us to determine the oxidation states and electronic environment of the elements in the outermost layers of the material. The Ni 2p\(_{3/2}\) spectra of all samples can be found in Fig. S5a, with the associated Cu 2p\(_{3/2}\) and Co 2p\(_{3/2}\) regions for the NiCu-
Sap and NiCo-Sap catalysts in Fig. S5b and S5c, respectively. Table 2 contains a summary of the main peaks found in Fig. S5. Prior to this analysis, all samples were reduced under the same conditions used before a reaction (850 °C, 1 hour, 20% H₂:80% N₂). As seen in both Fig. S5a and Table 2, there are several Ni oxidation states that exist following reduction and are seen in the deconvoluted spectra. The bands ca. 851-852 eV are characteristic of Ni⁰, while the bands at 852-854 eV are attributed to Ni²⁺ species interacting with the support [26, 45, 46]. The band centred at binding energy (BE) 857 eV, in the case of the NiCu-Sap catalyst, is attributed to Ni²⁺ as part of surface NiCu alloy species [47, 48]. This assignment is corroborated when considering the Cu 2p₃/₂ region that details a shift towards BEs associated with NiCu alloys [49]. The remaining bands are the shake-up satellite peaks associated with the previous species. However, the BE displayed in the NiCo-Sap catalyst at 855.48 eV is indicative of Ni³⁺ cations present [51, 52], characteristic of NiCo alloys [53].

The Cu 2p₃/₂ region in the NiCu saponite, Fig. S5b, shows two significant bands. One band at 932 eV can be assigned to the Cu⁺/Cu⁰ species, with the higher bands at 934, 940 and 943 eV attributed to the Cu²⁺ species and two shake up satellites, respectively [45, 54]. The main bands for Cu at 932 and 934 eV can be explained to be at higher binding energies than monometallic Cu as found in literature, due to the charge transfer from Cu to the partially empty d-band present in Ni and the oxidation of Cu [55, 56]. Such electronic interaction between the two metals has been theorised to contribute to increased catalytic activity since it results in an electronically rich metal-metal interface which is ideal for reactants activation [48, 49]. Furthermore, the Ni-Cu interface has been identified to be the active site for the forward and reverse water gas shift reactions by enhancing CO/CO₂ adsorption and suppressing methane production [50]. Additionally, it has been found that high compositional contents of Cu in a Cu-Ni alloy sufficiently increased the reducibility and mesoporosity of the structure to subsequently increase the catalytic activity [45].

Finally, the Co 2p₃/₂ spectrum for the NiCo saponite found in Fig. S5c details two main bands at 778 and 780 eV, which are attributed as Co³⁺ and Co²⁺, respectively [53]. While the other two bands are the associated shake-up satellites [57, 58]. Another key factor found in the data for this region, is that the splitting (spin-orbit coupling) energy between the Co2p₁/₂ and Co 2p₃/₂ orbitals (not shown) is approximately 15 eV, further indicating the coexistence of Co²⁺/Co³⁺ species [57].
Table 2. Binding energies of the Ni 2p3/2, Co 2p3/2 and Cu 2p3/2 regions for the reduced catalysts, as well as the Ni/Sap atomic ratios. (Sap=Al, Si and Mg)

| Catalyst   | Ni 2p3/2 (eV) | Co 2p3/2 (eV) | Cu 2p3/2 (eV) | Ni/Sap |
|------------|---------------|---------------|---------------|--------|
| NiSap      | 852.38        | 854.38        | -             | 0.058  |
| NiCuSap    | 852.48        | 854.58        | 857.08        | 932.38 | 0.056  |
| NiCoSap    | -             | 855.48        | 778.48        | 780.58 | 0.054  |

The estimated Ni/Sap atomic dispersions (Table 2) show very similar surface dispersions of the Ni over the saponite material regardless of the inclusion of Co or Cu. This is indicative of the homogeneous precipitation of the metal-adamantane carboxylates over the exfoliated clay layers during the hydrothermal synthesis of catalyst precursors. However, the slightly increased value for the Ni-Sap could indicate a slight enrichment of surface Ni on the Ni-Sap sample.

The textural properties of the active catalysts were analysed using N2 adsorption. Fig. 5 shows the adsorption isotherms of all the samples and surface properties are tabulated in Table 3. All the samples show type IV adsorption isotherm with the H4 hysteresis loop characteristic of mesoporous solids. Surface area of the catalysts calculated by the BET method and pore size and pore volume were calculated by BJH method by using the desorption branch of the isotherm. The NiSap catalyst shows 120 m²/g of surface area.

Figure 5. BET Isotherm plots for NiCoSap, NiCuSap and NiSap.
whereas, NiCuSap and NiCoSap show surface area of 85 and 87 m²/g, respectively, which indicates the nucleation of the second metal in the catalysts’ porous structure.

Ultimately, however, beyond the onset relative pressure of the loop, the isotherms confirm the presence of narrow or slit shaped mesopores within the material that are confirmed by the BJH analysis of the material (Table 3) confirming average pore diameters between 2-50 nm.

**Table 3.** Textural characteristics established for investigated catalysts, as calculated by BET (Surface Area) and BJH (Pore volume and diameter) analysis

| Sample          | $S_{\text{BET}}$ (m² g⁻¹) | $V_{\text{Pore}}$ (cm³ g⁻¹) | $D_{\text{Pore}}$ (nm) |
|-----------------|-----------------------------|-------------------------------|-------------------------|
| Ni-Saponite     | 120                         | 0.202                         | 7.1                     |
| NiCu-Saponite   | 85                          | 0.156                         | 7.9                     |
| NiCo-Saponite   | 87                          | 0.142                         | 7.7                     |
Figure 6. TEM images of NiCuSap (a, d), NiCoSap (b, e) and NiSap (c, f).

Freshly prepared catalysts were further characterised by electron microscopy and the TEM images are shown in Fig. 6. Clay layers of saponite are clearly identified supporting the metal/metal alloy nanoparticles in the images. Fig. 6a and d show monodispersed NiCu nanoparticles in the range of 15-20 nm homogeneously distributed over the clay layers. Fig. 6b and e show the NiCo nanoparticles with many of them having sizes between 10-15 nm. A small percentage of the NiCo nanoparticles are however larger size measuring about 30-50 nm. The bigger nanoparticles in NiCo could be due to aggregation of nanoparticles on the surface of the clay sheets. Similar observation was made for NiSap catalyst (Fig. 6c and f). Different shades of the nanoparticles could indicate that they are present at varying depths in the clay matrix. The lighter shaded, smaller nanoparticles in Fig. 6 could be the ones formed due to restricted growth in the clay interlayers at greater depths. Whereas, the nanoparticles formed on the surface of the clay layers might have undergone greater extent of agglomeration resulting in a small percentage of larger particles. Excluding which, the average particle sizes of monometallic Ni-nanoparticles in the catalyst varied between 10-15 nm. It is worth noting that,
larger nanoparticles are less abundant in the NiCuSap catalyst (Fig. 6a and d) in comparison to the other two catalysts.

![STEM Image](image)

**Figure 7.** STEM image (a) and elemental maps for Ni, Cu, Mg, Al, Si and C of NiCuSap catalyst.

NiCuSap was further characterised using STEM to map the active sites distribution on the clay support. The electronic image of the freshly prepared NiCuSap catalyst is shown in Fig. 7a, along with the corresponding elemental maps of Ni, Cu, Mg, Al, Si and C. The NiCu-alloy nanoparticles are bright spots and the grey hazy matrix belongs to saponite clay sheets in the STEM image (Fig. 7a). The image also depicts a homogeneous dispersion of the NiCu-alloy nanoparticles in the saponite clay matrix. Complementing Ni and Cu elemental maps indicate the presence of both Ni and Cu in each of the nanoparticles. Saponite support displays coherent distribution of Mg, Al and Si accounting for homogeneously formed saponite clay layers. *In situ* generated carbon in the freshly prepared catalysts was found to be distributed homogeneously over the saponite clay layers. The presence of carbon in the catalysts was also indicated in the Raman analysis as discussed earlier.

3.2. **Catalytic Testing for RWGS Reaction**

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All saponite based catalysts were tested using a reactant ratio favourable for both the RWGS and methanation reactions and a WHSV 15 L_{g.cat}^{-1}h^{-1} that was applied across different temperatures as mentioned in the experimental section. Fig. 8 shows the conversion and selectivity results of this testing and clearly depicting the competitive nature of both the RWGS and CO₂-methanation reactions. The monometallic NiSap catalyst favours the methanation reaction, attaining 83 % CH₄ selectivity at 450 °C. In fact, as pointed out in the XPS section, the monometallic sample has greater exposition of Ni on the surface acting as active centres for methanation. The NiCoSap material displays an intermediate behaviour with good levels of CO₂ conversion and higher selectivities to CO compared to the monometallic sample. As for the NiCuSap catalyst a highly interesting trend was observed, specifically due to preferential formation of CO over CH₄, even at lower temperatures, where typically the methanation reaction is the dominant process. This is seen in the selectivity plots, Fig. 8b and c, where there is little to no methane produced, while CO is being produced in abundance. Overall the Ni-Cu catalyst is the best material within the studied series and hence we have compared its performance with reference systems. As shown in Table 4 the NiCuSap shows either markedly improved or comparable performance as a number of transition metal and noble metal catalysts reported recently [22, 26, 31, 59, 62-64] using the same temperature window and reaction mixture (CO₂:H₂ 1:4). Only the bimetallic Fe-Ni catalysts reported in [26] outperforms our CO₂ conversion levels but the selectivity of the material is much lower than that exhibited by our Ni-Cu catalysts. Hence the Ni-Cu/saponite catalyst represents an excellent balance activity/CO selectivity when compared with benchmark materials. The homogenous distribution and high dispersion of the Ni-Cu active centres shown in the STEM study, along with the Ni-Cu electronic interaction discussed in the XPS section, can explain the excellent performance of this sample. Cu suppresses the methanation activity of Ni and the Ni-Cu ensemble is an advanced active phase for the RWGS reaction, leading to high levels of CO₂ conversion in the whole temperature range and remarkable selectivity levels towards CO. In fact the presence of Cu opens up the possibility to conduct the RWGS reaction via redox and/or formate mechanism as previously reported elsewhere thus favouring the CO route over the CH₄ pathway [65]

In any case, the superior behaviour of our catalysts compared to reference materials is indeed a very encouraging result and showcases the viability of low cost nature inspired multicomponent catalysts for the reverse water gas shift process. Due to this behaviour, the
NiCuSap catalyst was selected for a stability study at 500 °C as this temperature indicated significant conversion at lower temperature for the RWGS reaction, while not reaching equilibrium.

**Table 4.** Comparative table detailing the present work catalysts against a number of materials reported in the literature

| Material          | Temperature (°C) | WHSV (L/gcat h) | CO₂ Conversion (%) | CO Selectivity (%) | Ref          |
|-------------------|------------------|-----------------|---------------------|--------------------|--------------|
| NiCu-Saponite     | 500              | 15              | 53                  | 89                 | This work    |
| Ni-Saponite       | 500              | 15              | 57                  | 16                 | This work    |
| NiCo-Saponite     | 500              | 15              | 49                  | 37                 | This work    |
| NiFe/CeAl         | 500              | 30              | 65                  | 18                 | [26]         |
| β-Mo₂C            | 500              | 12              | 56                  | 80                 | [56]         |
| Fe/Al₂O₃          | 500              | 12.5            | 40                  | 92                 | [22]         |
| Pt/Mullite        | 500              | 30              | 16                  | 85                 | [59]         |
| Pt/KLTL Zeolite   | 500              | 30              | 12                  | 97                 | [60]         |
| 5wt% Cu/β-Mo₂C    | 500              | 30              | 20                  | 100                | [61]         |

**Figure 8.** Temperature screening results for (a) CO₂ conversion, (b) CO selectivity and (c) CH₄ selectivity for NiCoSap, NiCuSap and NiSap catalysts.

The results shown in Fig. 9 clearly illustrate this catalysts’ resistance to deactivation, maintaining considerable conversion (ca. 55% CO₂ conversion) and high selectivity for CO
(ca. 80 %) for over 89 hours of continuous reaction. Furthermore, these results are a considerable enhancement over recently published materials.

The suppression of methanation by copper containing materials has been previously reported by our team in the forward WGS reaction [60, 61]. However, the potential of this alloy for the reverse water gas shift process is still under explored. The enhanced selectivity to CO at low temperatures is an encouraging result to achieve the successful coupling of RWGS with downstream processes such as Methanol synthesis and Fischer-Tropsch which typically take place at around 250-350 °C. This way we could close the cycle: CO₂ conversion to fuels and chemicals in a two step-process with the RWGS as front unit and the F-T or methanol conversion reactors as second unit to produce the upgraded end products.

3.3 Characterization of Spent Catalysts

The x-ray diffraction patterns of the spent catalysts from the temperature screening experiments are shown in Fig. 10. All the diffractograms display peaks at around 28.2°, 31.05° and 35.5° 20 due to saponite support. Additionally, the expected peaks for the loaded
metal/metal alloys at around, 44°, 51° and 76° remain unaltered in the spent catalysts in comparison to the freshly prepared catalysts. No phase segregation of the metal alloys was observed after the screening tests and therefore the PXRD patterns of the spent (Fig. 10) and the freshly prepared catalysts are identical. While the results of the Scherrer equation from the respective PXRD patterns of both the fresh and the spent catalysts (after temperature screening experiment) displays no change, indicating almost no agglomeration of the active metal/metal alloy nanoparticles; due to the overlap of the crystal peaks, it is impossible to determine the level of sintering present for the individual components. This explains partially the continuous activity of NiCuSap catalyst for 89 hours with negligible loss in activity. Presence of crystalline carbon peaks could not be found, making any carbon formation amorphous. The stability pattern of the catalyst is characteristic of the in situ generated carbon stabilized metal nanoparticle catalysts [31]. However, in this case, saponite support and the metal alloy combination has added to the conversion levels of CO₂ and improved selectivity of the catalyst for RWGS reaction.

Figure 10. PXRD patterns of the spent (a) NiSap, (b) NiCuSap and (c) NiCoSap catalysts.

Following the temperature screening experiments, the spent sample was analysed using a JEOL 7100F Scanning Electron Microscope (SEM) with an Energy Dispersive X-Ray spectroscope (EDX) to determine both active phase dispersion and the presence and type of coking. Fig. S6, S7 and S8 present the SEM/EDX results for the post reaction NiCuSap, NiCoSap and NiSap samples, respectively. These results show clearly well dispersed active phase with some small amount of amorphous carbon present on the surface of the spent catalysts, which is in good agreement with the lack of crystalline carbon peaks in the spent materials XRD diffractograms. Fig. S8 clearly details the presence of Ni as small particles on the surface of the material, while Fig. S6 and S7 show that the Ni is highly dispersed throughout the catalyst.

Combusting the spent material under air from room temperature to 900°C at 10 °C/min revealed several zones (Fig. 11). Each sample underwent an initial loss between room temperature (RT) – 160°C that is attributed to free water loss. Each sample then displayed a significant weight gain (+5-14 wt %) in between 200-450 °C for NiCuSap and
NiCoSap that is attributed to the oxidation of the metals. The same weight gain zone for the NiSap occurred at the slightly higher zone of ca. 275-500 °C.

The spent NiCoSap catalyst displayed a two-step weight loss totalling 3.8 wt% which is attributed to the loss of surface carbon and then engrained carbon. In a similar fashion, the spent NiCuSap catalyst details a one-step weight loss (1.5 wt %), which is also attributed to the loss of surface carbon. These conclusions are supported by the presence of an exothermic heat flow curves for the oxidation of the metals and the associated oxidation of the amorphous carbon (not shown). The weight gain of these materials being related to metallic oxidation is further supported by the curve displayed for the NiSap material, which details a much smaller increase owing to its monometallic loading. Interestingly, however, the NiSap material did not display any weight loss at higher temperatures. In any case the TGA profiles corroborate the absence of crystalline carbon deposits in good agreement with XRD. This observation along with the lack of metallic sintering validate that these “nature inspired” catalysts developed in this work are not only highly active, but also very robust for the RWGS reaction.

![Figure 11. Comparative oxidation TGA curves for the spent NiCuSap, NiCoSap and NiSap catalysts.](image)

**Conclusions**

This work demonstrates the viability of nature inspired transition metal based catalyst for gas phase CO₂ upgrading via RWGS. Aqueously exfoliated saponite magnesio-
aluminosilicate layers have been effectively used to support the synthesis of metal adamantane-carboxylates under hydrothermal conditions. The catalyst precursors underwent controlled decomposition under hydrogen atmosphere to produce *in situ* generated carbon stabilised saponite supported metal alloy catalysts. All the as prepared catalysts (mono: Ni and bimetallic: Ni-Cu and Ni-Co) display excellent activity levels in the RWGS process outperforming the activity levels exhibited by reference catalysts reported in literature. Interestingly, the undesired parallel reaction – the Sabatier process – which typically is the dominant reaction in the low temperature window can be suppressed using Ni-Cu alloys as active phases. Indeed, the bimetallic Ni-Cu system is the best performing material within the studied series with an outstanding balance activity/CO selectivity in addition to be a very stable catalysts for long term runs. The electronic interaction Ni-Cu evidenced by XPS contributes to this exceptional behaviour. Indeed, such a close metal-metal contact results and electronically rich Ni-Cu interface which is ideal for CO$_2$ activation. No signs of carbon deposition due to the reaction, nor metallic sintering were observed, explaining the enhanced stability of this material.

Considering a potential application where the RWGS unit is coupled to a downstream process using syngas such as Fischer-Tropsch or methanol synthesis – the obtained results are very encouraging since our Ni-Cu catalyst is very active and selective towards CO in the low temperature range minimising the temperature gap between RWGS and the Fischer-Tropsch or methanol unit. In other words, the catalysts developed in this study may facilitate the integration of a RWGS reactor with a syngas convertor – such an integrated dual system would enable the direct conversion of CO$_2$ to added value chemicals.

declaration of interests

The authors declare that they have no competing interests.

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