Co-Fe Nanoparticles Wrapped on N-Doped Graphitic Carbons as Highly-Selective CO\textsubscript{2} Methanation Catalysts

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Abstract

Pyrolysis of chitosan containing various loadings of Co and Fe renders Co-Fe alloy nanoparticles supported on N-doped graphitic carbon. TEM images show that the surface of Co-Fe NPs are partially covered by three or four graphene layers. These Co-Fe@(N)C
samples catalyze the Sabatier CO\(_2\) hydrogenation, increasing activity and CH\(_4\) selectivity with the reaction temperature in the range of 300 to 500 °C. Under the optimal conditions, a CH\(_4\) selectivity of 91 % at 87 % CO\(_2\) conversion was reached at 500 °C and a space velocity of 75 h\(^{-1}\) under 10 bar. The Co-Fe alloy nanoparticles supported on N-doped graphitic carbon are remarkably stable and behave differently as an analogous Co-Fe catalyst supported on TiO\(_2\).

**INTRODUCTION**

Greenhouse gas emissions are considered responsible for the anthropogenic influence on global warming.\(^1\) To diminish atmospheric emissions, there is much current interest in utilizing CO\(_2\) as feedstock for processes that can be carried out at the very large scale. These new processes should be able to consume very large CO\(_2\) volumes to make an impact avoiding CO\(_2\) emissions.\(^2\)-\(^4\) Hydrogenation of CO\(_2\) to obtain hydrocarbons is an exothermic process that can produce useful fuels and chemicals,\(^5\)-\(^6\) provided that the H\(_2\) consumed in the process has a neutral CO\(_2\) footprint, as the green hydrogen obtained from water electrolysis.\(^7\) Hydrogenation of CO\(_2\) to methane, also known as the Sabatier reaction,\(^8\)-\(^9\) is one of these possible reactions that can be carried out at huge scale and has the advantage of making possible to use the existing natural gas distribution network and infrastructure.

CO\(_2\) methanation requires active and selective catalysts.\(^6\) Typical catalysts for this reaction include earth-abundant transition metal nanoparticles (MNPs), including Ni, Fe and Cu, supported on large surface area inorganic supports.\(^6\),\(^9\) Among these supports, metal oxides are those most commonly used. However, there is an increasing interest in using graphene materials and related large area graphitic carbons,\(^10\)-\(^11\) since the catalytic activity of MNPs supported on defective graphenes may exhibit a unique activity. It is known that MNPs can
anchor on defects and dopant positions, establishing strong metal-defective graphene interaction that can result in charge transfer between the graphene sheet and MNPs,\textsuperscript{12-14} tuning the catalytic activity.

In a series of papers, it has been reported that upon pyrolysis of chitosan adsorbing metal salts, the formation of MNPs supported on N-doped defective graphene sheets and N-doped graphitic carbons can be obtained.\textsuperscript{15-17} The process is straightforward since chitosan and related polysaccharides exhibit a high capacity to adsorb metal salts from water.\textsuperscript{18} In addition, upon pyrolysis, chitosan as a homopolymer of glucosamine acts simultaneously as a source of C and N, resulting in the formation of N-doped, turbostratic graphitic carbons that can be exfoliated to defective graphenes.\textsuperscript{19}

Based on these precedents, herein the preparation from chitosan of Co-Fe alloy NPs wrapped on N-doped graphitic carbon [Co-Fe@(N)C] exhibiting a remarkable activity and stability as CO\textsubscript{2} methanation catalysts are reported. The performance of these Co-Fe alloy NPs on N-doped graphitic carbon improves those of similar Co-Fe alloys supported on TiO\textsubscript{2}, illustrating the advantage of (N)C as support. Prior studies in the literature have shown the importance of the metal-support interaction and that Co NPs supported on Al\textsubscript{2}O\textsubscript{3} undergo fast deactivation as catalysts in the Sabatier reaction.\textsuperscript{6}

RESULTS AND DISCUSSION.

As indicated in Scheme 1, the samples Co-Fe@(N)C under study were prepared by two different procedures. Thus, samples 1-3 (Scheme 1, a) were prepared in the form of quasi-spherical submillimetric beads by co-precipitation with NaOH of an aqueous chitosan solution acidified by HOAc containing also the appropriate amounts of Co(OAc)\textsubscript{2} and Fe(OAc)\textsubscript{2}. Medium and high molecular weight chitosan is soluble in acidic aqueous solutions

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but precipitates under neutral or basic conditions. Subsequently, the chitosan spheres containing Co$^{2+}$ and Fe$^{2+}$ salts were dried by a gradual exchange of H$_2$O by EtOH and final supercritical CO$_2$ extraction of ethanol. This procedure has previously been reported as resulting in a highly-porous, large surface area chitosan aerogels.\textsuperscript{20-21} Final pyrolysis at 900 °C converts the chitosan beads into turbostratic graphitic carbon, accompanied by the simultaneous formation of metallic Co-Fe alloy NPs. Chemical reduction of Co$^{2+}$ and Fe$^{2+}$ ions occurs during the pyrolysis simultaneously with chitosan graphitization due to the reductive conditions of the process derived from the absence of oxygen.\textsuperscript{22-23}

In an alternative procedure also indicated in \textbf{Scheme 1}, Co-Fe@(N)C samples 4 and 5 were prepared by first forming the chitosan beads by NaOH precipitation of acidic aqueous chitosan solution, then, exchanging H$_2$O by EtOH before adsorbing Co(OAc)$_2$ and Fe(OAc)$_2$ from EtOH solution. Subsequently, Co$^{2+}$ and Fe$^{2+}$ were reduced by NaBH$_4$ in EtOH before pyrolysis. For the sake of comparison, one additional sample using TiO$_2$ as support was also prepared by wet impregnation of TiO$_2$ with an aqueous solution of Co(OAc)$_2$ and Fe(OAc)$_2$, followed by drying and H$_2$ reduction of the resulting powder at 600 °C.

\begin{center}
\textbf{Scheme 1.} Pictorial illustration of preparation procedures. a) Samples 1-3 being \textit{i}) Precipitation in NaOH; \textit{ii}) water/EtOH exchange; \textit{iii}) CO$_2$ supercritical drying.
\end{center}
b) Samples 4-5 being i') Precipitation in NaOH; ii') water/EtOH exchange; iii') metal salt adsorption; iv') CO₂ supercritical drying.

The list of samples, their most important analytical data and Co-Fe NP size distribution are collected in Table 1, while supporting information (Table S.1) indicates the exact amounts of chitosan, Co(OAc)₂ and Fe(OAc)₂ used in the preparation of each of the five Co-Fe@(N)C samples.

| Sample No. | Co (wt.%)<sup>a</sup> | Fe (wt.%)<sup>a</sup> | Total Co+Fe content (wt.%)<sup>a</sup> | C (wt.%)<sup>b</sup> | N (wt.%)<sup>b</sup> | Average particle size (nm)<sup>c</sup> |
|------------|-----------------|-----------------|----------------------------------|--------------|--------------|-------------------------------|
| 1          | 4.9             | -               | 4.9                              | 85.85        | 1.48         | 9.5±2                         |
| 2          | 12.0            | 5.0             | 17.0                             | 76.80        | 1.21         | 6.9±2                         |
| 3          | 13.6            | 5.2             | 18.8                             | 72.36        | 0.31         | 9.7±5                         |
| 4          | 13.1            | 4.6             | 17.7                             | 64.37        | 0.75         | 13.3±4                        |
| 5          | 17.5            | 4.3             | 21.8                             | 63.91        | 1.05         | 11.2±3                        |

<sup>a</sup> Determined by ICP-AES analysis after dissolving the metals in <i>aqua regia</i>; <sup>b</sup> It is assumed that the rest to 100 % is residual oxygen; <sup>c</sup> Determined by DF-TEM.

As it can be seen in Table 1, sample 1 contains only Co, while the other samples 2-5 contain a similar Fe content between 4.3 to 5.0 wt.%, varying in the Co content from 12.0 to 17.5 wt.%. Of note is that the exact metal content of samples 1-5 is difficult to predict beforehand in the adsorption step due to high weight loss resulting in the pyrolysis converting moist
chitosan into the (N)C. Importantly, samples 1-5 contain a residual weight percentage of N from the original chitosan composition that ranges from 0.31 to 1.48 wt.% (see Table 1). In previous studies, it has been found that the N content of graphitic carbon derived from chitosan can vary from 6.5 wt. % to a negligible value depending on the pyrolysis conditions and the presence of metals that can promote graphitization.17, 24

X-ray diffraction (XRD) patterns of samples 1-5 show that they are constituted by metallic Co and Fe, mainly in the fcc (sample 1) or bcc, accompanied by less intense peaks of the fcc (samples 2-5). No other peaks attributable to metal oxides were recorded in these patterns, indicating that, as expected, Co$^{2+}$ and Fe$^{3+}$ ions have become reduced to their metallic state during the pyrolysis process. Previous studies have widely documented that pyrolysis of carbon precursors results in the chemical reduction of transition metals,25-28 including Fe.29

To determine if the Co and Fe elements present in the samples are independent Co and Fe particles or they are alloyed, experimental XRD data were analyzed by Rietveld refinement. As an example, Figure 1 shows the fitting of the Rietveld analysis and the experimental data. However, although this XRD analysis supports the formation of Co-Fe alloy, the similarity between the cell parameters of metallic Co and Fe makes necessary additional confirmation by transmission electron microscopy to address this issue.
Transformation of chitosan into N-doped graphitic carbon was assessed by Raman spectroscopy. Graphene and graphitic carbons present in Raman spectroscopy three characteristic vibration bands at wavenumbers between 3000 and 2600, 1590 and 1350 cm\(^{-1}\) corresponding, respectively, to overtones, G and D bands. Figure 2 shows representative Raman spectra for the Co-Fe@(N)C samples under study. The width of the G and D peaks and their relative intensity (I\(_G\)/I\(_D\)) are taken as quantitative indicators of the quality of the graphene layers. In the present case, the G and D peaks are notably narrower than those previously reported in the pyrolysis of chitosan at 900 °C, probably reflecting the influence of Co-Fe NPs promoting a better graphitization of the (N)C residue. This proposal would be in agreement with the previously commented lower than expected N content of the samples indicated in Table 1. In addition, particularly for samples 1-3, the Raman spectra show a
narrow 2D peak in the high-frequency region at about 2700 cm\(^{-1}\). Observation of narrow 2D peaks is associated generally with the presence of few layers of graphene stacking since this 2D peak becomes broader and eventually disappears as the number of stacked graphene layers increases. Thus, Raman spectra indicate that the carbon residue, particularly in samples 1-3 is constituted by the stacking of a few N-doped defective graphene layers.

![Raman spectra](image)

**Figure 2.** Raman spectrum of the samples 1-5 recorded upon 514 nm laser excitation.

The morphology of the materials was determined by field emission scanning electron microscopy (FESEM). It seems that the known morphology of chitosan aerogels constituted by the agglomeration of cotton-like, fluffy fibrils are mostly preserved in the pyrolysis during the transformation of chitosan into (N)C residue. **Figure 3** shows representative FESEM images of the samples under study in which the loose, coral-shape, spongy morphology of the samples with considerable macroporosity can be observed. The presence of MNPs could
not be visualized by FESEM, meaning that these MNPs should be smaller enough to not become visualized at the 100 nm scale of the technique.

**Figure 3.** FESEM images of samples 1-5. a, b: sample 1; c, d: sample 2; e, f: sample 3; g, h: sample 4 and i, j: sample 5.

The presence of Co-Fe NPs supported on graphene layers of a few micrometers dimensions could be clearly detected in transmission electron microscopy (TEM) images of the samples after ultrasound dispersion of the black carbon powders, both in bright and dark fields (DF). **Figure 4** shows selected images of the samples under study, while supporting information (Figure S.1) contains a more complete set. The particle size distribution and the average size was determined by measuring a statistically significant number of MNPs. These values are collected in **Table 1**, while the corresponding histograms are inserted in the TEM images. Average Co-Fe particle size between 6.9 and 13.3 nm with somewhat broad size distribution were estimated from these images. From the high-resolution images, measurement of a fringe distance of 0.22 nm corresponding to the 110 distance of the bcc phase indicates that the Co-
Fe NPs correspond to a random alloy since these values are between those corresponding to independent Co and Fe bcc phases.

Figure 4. DF-TEM images of samples 1-5 and HRTEM images of sample 4. a, b: sample 1; c, d: sample 2; e, f: sample 3; g, h, k, l: sample 4 and i, j: sample 5.

High-resolution TEM images in bright field also revealed that Co-Fe NPs are wrapped by a few (three and four) layers of N-doped graphene characterized by its typical 0.34 nm interplanar distance. It appears that this wrapping is not complete, but covers partially the surface of the Co-Fe NP. To illustrate this important point that can serve to understand the role of (N)C on the catalytic activity, (Figure 4, k, l) has marked a representative case, while additional images can be found in the supporting information (Figure S.2). As commented in the introduction, theoretical calculations on models have suggested that graphene can donate charge density to the Co-Fe NP and this charge transfer enriching the electron density at certain atoms of the MNP in contact with graphene basal plane can act as catalytic sites exhibiting stronger CO$_2$ binding.
Catalytic activity

The catalytic activity of samples 1-5 for CO\textsubscript{2} methanation was tested in a pressurized fixed-bed, stainless steel reactor in the range of temperatures from 300 to 500 °C. Each catalyst was submitted to catalytic tests in which the reactor temperature is increased in 50 °C increments with a dwell time of 1 h. The activity data at each temperature was the average of three analysis of the reaction mixture performed at 30, 45 and 55 min. For all data, the variation among the three analyses was lesser than 5 %. Preliminary controls at 500 °C in the absence of any catalyst or using (N)C without any metal as catalyst showed a CO\textsubscript{2} conversion of 6 and 12.9 %, respectively, methane being the main product with a selectivity over 95 %. Previous reports in the literature have shown that N-doped graphene can act as a methanation catalyst,\textsuperscript{30} although the activity measured in our conditions was much lower than that measured for the Co-Fe@(N)C samples.

All samples Co-Fe@(N)C exhibit a remarkable catalytic activity for CO\textsubscript{2} hydrogenation. The main product was CH\textsubscript{4}, accompanied by a lesser percentage of CO. The formation of minute, but detectable, amounts of C\textsubscript{2+} products constituted by ethane, propane, butane, ethylene and propylene were also observed. Thermodynamic calculations on CO and CO\textsubscript{2} hydrogenation, validated in the case of CO, indicate that under the present reaction conditions the equilibrium should be reached at very high CO\textsubscript{2} conversion with 100 % selectivity to CH\textsubscript{4} up to temperatures of 500 °C.\textsuperscript{31} Therefore, although in some cases close to the equilibrium, the data achieved in the present study is not limited by equilibrium considerations. As a general trend of all the samples, CO\textsubscript{2} conversion and CH\textsubscript{4} selectivity increase with the temperature, the highest values in the temperature range under study being measured at 500 °C. Figure 5 summarizes the results obtained for the Co-Fe@(N)C samples...
under study, while supporting information (Figures S.3 and S.4, Tables S.2 to S.7) gathers the full set of data for all the catalytic study.

Figure 5. CO₂ methanation for samples 1-5 at 500 °C, under the same conditions. (Reaction condition: H₂/CO₂ ratio of 7, total flow 4 mL/min, 10 bar, 40 mg catalyst.)

As it can be seen in Figure 5, CO₂ conversion and CH₄ selectivity varied also depending on the sample composition. It was observed that sample 1 containing lesser total metal loading reached lower CO₂ conversions and exhibits higher unwanted CO percentages, compared to the rest of the samples that contain Co-Fe alloy. On the other hand, the catalytic activity of sample 5 that contained a somewhat higher total metal percentage was lower than for samples 2-4. Worth noting is the observation of a high percentage of about 20% of C₂+ products for samples 3 and 4 at 400 °C for CO₂ conversion above 60%.

It was determined that the best performing catalyst was sample 4 that reached 87% CO₂ conversion with a CH₄ selectivity of 91% operating at 500 °C and a space velocity of 75 h⁻¹.
at 10 bar. The better performance of sample 4 is observed in spite of the notably larger particle size compared particularly with sample 2 that has a similar composition, but smaller particle size. This different behavior between samples 2 and 4 is most probably due to the different preparation procedures. When the different total metal content of the samples is taken into consideration and turnover frequencies are considered as the figure of merit of the catalytic performance, sample 1 is the best performing due to its low metal content (TOF 25.7 s⁻¹), while the other samples have similar TOF values ranging from 8.7 s⁻¹ for sample 4, 8.5 s⁻¹ for sample 2, 7.9 s⁻¹ for sample 3, and 7.0 s⁻¹ for sample 5.

Stability of sample 4 was assessed by performing a long run 30 h experiment at 500 °C observing a constant CO₂ conversion and product distribution. After the 30 h reaction at 500 °C, the sample was screened again for its activity at each temperature between 300 and 500 °C, observing a consistent reproducibility in CO₂ conversion values and product distribution.

Finally, the influence of (N)C as support of Co-Fe alloy NPs was assessed by comparing the activity data of samples 1-5 with that of Co-Fe NP supported on TiO₂ (see Table S.7 in Supporting information). In this case, the main product under the same reaction conditions was CO with a selectivity of 92.8 % at a CO₂ conversion of 29.8 % measured at 450 °C. Table S.7 contains the full catalytic data for Co-Fe/TiO₂ as a function of the reaction temperature.

CONCLUSIONS

The present study discloses the two different preparation procedure of Co-Fe alloy NPs supported on N-doped graphitic carbon in which the Co-Fe NPs are partially wrapped by two to four graphene layers. These Co-Fe@(N)C samples exhibit catalytic activity for the Sabatier methanation of CO₂, reaching CH₄ selectivity over 90 % at high CO₂ conversion
values over 85 %. This catalytic activity contrasts with that of similar Co-Fe NPs supported on TiO$_2$ for which CO is the main product. These catalysts Co-Fe@(N)C appear to be stable for long time runs. Overall, the present study shows the potential of chitosan to form graphitic carbon supported metal catalysts with remarkable activity and stability.

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