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COMMUNICATION

Effect of nanostructured ceria as support for the iron catalysed hydrogenation of CO₂ into hydrocarbons

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This paper demonstrates the key role of the property-structure relationship of the support on iron/ceria catalysts on the hydrocarbon selectivity and olefin-to-paraffin ratio for the direct hydrogenation of carbon dioxide into hydrocarbons. The effect is directly related to the reducibility of the different nanostructured ceria supports and their interaction with the iron particles. Herein, we demonstrate that the iron-based catalysts can be modified not only by the addition of promoters, commonly reported in the literature, but also by careful control of the morphology of the ceria support.

The environmental impact of a continuous release of CO₂ into the atmosphere is urging the scientific community to find novel ways of converting CO₂ waste into valuable chemicals^{1, 2}. Implementation of oxyfuel combustion on power stations produces highly concentrated (> 98 %) CO₂ streams for carbon capture and storage (CCS). Alternatively, these waste streams can be used as chemical feedstock overcoming the dilution problems associated to the recovery of CO₂ from the atmosphere^{3, 4}. The last decades have witnessed a plethora of studies to unlock the potential of carbon dioxide as a raw material in the synthesis of carboxylates, carbonates, carbamates, C-1 molecules such as formic acid and methanol as well as fuels^{2, 5, 6}. Amongst them, hydrogenation of CO₂ either through the methanol^{7, 8} or the non-methanol^{5, 9} mediated routes is a promising and flexible pathway for the production of commodity chemicals such as methanol, methane, and C₂₊ hydrocarbons (HCs) currently produced from petroleum-based sources. Specifically, the non-methanol mediated tandem system conversion of CO₂ into a more reactive CO moiety via reverse water gas shift reaction (RWGS) followed by

conventional Fischer-Tropsch (F-T) for the formation of hydrocarbons is an attractive and highly prized route for fuel production¹⁰. In this case, cobalt and iron based catalysts are the most studied systems¹¹. The former, widely used in Fischer-Tropsch synthesis, highly increases its methanation ability when the feed is shifted from syngas to a CO₂/H₂ mixture¹²⁻¹⁴. On the other hand, iron-based catalysts are attractive due to the olefinic hydrocarbons formed during F-T¹⁵, although their RWGS activity is considerably lower than the cobalt-based systems. In any case, the initial iron phases for the reduced fresh catalyst, mainly α -Fe and Fe₃O₄ are believed to be transformed under reaction conditions into an amorphous, and probably oxide, iron phase, active for the RWGS reaction⁵. Additionally, recent studies have confirmed that iron carbide species¹⁶, and in particular Fe₅C₂, act as active sites for the production of olefins and long hydrocarbons (C₅⁺) in the hydrogenation of CO via the Fischer-Tropsch process¹⁷⁻¹⁹. As iron-only catalysts tend to have high selectivities towards methane, a great effort has been focused on the use of promoters to enhance hydrocarbon formation. Metal alkali ions such as Na⁺, K⁺ or Cs⁺ decrease the hydrogenation ability of the iron active sites, decreasing the selectivity to methane and lower paraffins while also increasing the conversion of CO₂ and the chain-growth probability²⁰. In particular, K⁺ favours the re-oxidation of Fe during the reaction²¹. The addition of manganese acts not only as an electronic modifier but also as a structural promoter with similar effects^{22, 23}. Less attention has been paid to the effect of the support on the CO₂ hydrogenation reactivity although scattered screening studies demonstrate that it can have a clear effect not only in the activity but also in the selectivity²⁰. The effect of the support morphology on the activity and selectivity has been previously demonstrated for other systems such as WGS²⁴ or oxidation reactions^{25, 26}. Specifically, a considerable catalyst development in the last years has been based on the effect of nanostructuring of ceria in its reducibility²⁷ and its interaction with metal nanoparticles²⁸. This paper presents for the first time the effect of the morphology of the support at the nano-scale of iron/ceria catalysts on the resulting activity to provide

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Table 1: Catalytic performance of 20 wt.% Fe supported on nanostructured ceria for the hydrogenation of CO₂

| Catalyst | Reaction temperature / °C | CO ₂ conversion / % | Selectivity CO / % | Selectivity to HCs / % | Hydrocarbon selectivity / % | | | | | Olefin/paraffin ratio |
|--|---------------------------|--------------------------------|--------------------|------------------------|-----------------------------|--------|------|-------|-----|-----------------------|
| | | | | | CH ₄ | C2-4 = | C2-4 | C5+ = | C5+ | |
| 20wt.% Fe / CeO ₂ particles | 260 | 11.6 | 100.0 | 0.0 | 0 | 0 | 0 | 0 | 0 | - |
| | 300 | 17.3 | 98.3 | 1.8 | 100.0 | 0 | 0 | 0 | 0 | - |
| | 350 | 14.8 | 93.2 | 7.4 | 78.4 | 15.0 | 6.6 | 0 | 0 | 2.3 |
| | 390 | 26 | 94.6 | 6.8 | 76.6 | 18.1 | 5.3 | 0 | 0 | 3.4 |
| 20wt.% Fe / CeO ₂ rods | 260 | 7.5 | 78.7 | 21.3 | 78.5 | 1.2 | 15.6 | 0.6 | 2.7 | 0.1 |
| | 300 | 10.5 | 67.6 | 32.4 | 77.3 | 1.9 | 19.4 | 0.2 | 0.4 | 0.1 |
| | 350 | 17.2 | 64.5 | 35.5 | 77.1 | 8.0 | 14.2 | 0.2 | 0.2 | 0.6 |
| | 390 | 20.6 | 61.2 | 38.8 | 80.6 | 12.3 | 6.2 | 0.4 | 0.2 | 2.0 |
| 20wt.% Fe / CeO ₂ cubes | 300 | 9.1 | 74.7 | 25.3 | 73.3 | 13.1 | 13.6 | 0.0 | 0.0 | 1.0 |
| | 350 | 15.2 | 72.4 | 27.6 | 68.1 | 20.2 | 8.3 | 1.2 | 1.8 | 2.1 |
| | 390 | 18.9 | 73.5 | 26.5 | 75.5 | 18.2 | 4.0 | 1.2 | 0.7 | 4.1 |

Reaction conditions: 0.3 g of catalysts pre-reduced at 400 °C under 50 mL min⁻¹ H₂ flow. Inlet gas: 8 mL min⁻¹ of 3:1 H₂/CO₂ ratio. GHSV: 200 h⁻¹

The experimental error associated to the analysis is < 4%.

insights of the role of the metal-support interaction on the CO₂ hydrogenation system.

A series of nanostructured ceria materials were synthesised using a hydrothermal method. The morphology at the nanoscale is modified by varying the synthetic conditions²⁵. Pure ceria nanoparticles (~ 5nm) are formed at a NaOH concentration of 5M at 70 °C. Increasing the base concentration to 10 M and the temperature (100 °C) leads to ceria rods with an average diameter of 7 nm and assorted lengths between 20 – 80 nm. Ceria cubes with sizes between 20 – 100 nm were synthesised at 180 °C in a base concentration of 15 M. Full characterisation can be found elsewhere²⁵.

Fe(NO₃)₃·9H₂O as the precursor prior being reduced at 400 °C under a hydrogen flow. Figure 1 shows representative TEM pictures of the different Fe/CeO₂ catalysts. It can be observed that the support morphology is maintained after the iron impregnation and reduction. Nanoparticulated ceria present

dimension between 5-15 nm, ceria rods have diameters between 5 – 15 nm with assorted lengths and ceria nanocubes have dimensions between 40 – 100 nm. Size distributions of the bare ceria support can be found in our previous studies²⁶. In all cases, iron nanoparticles are not easily identified due to the similarity of contrast with the ceria.

The catalysts were tested in the direct hydrogenation of carbon dioxide into hydrocarbons under different reaction conditions (Table 1). All 20 wt.% Fe nanostructured catalysts present comparable CO₂ conversions which increase as the reaction temperature increases. However, considerable differences are observed in the hydrocarbon (HC) and CO selectivities. Fe supported on ceria particles presents much lower hydrocarbon formation than the other two catalysts, being the Fe/ceria rods the catalyst with higher hydrocarbon conversion for a given reaction temperature.

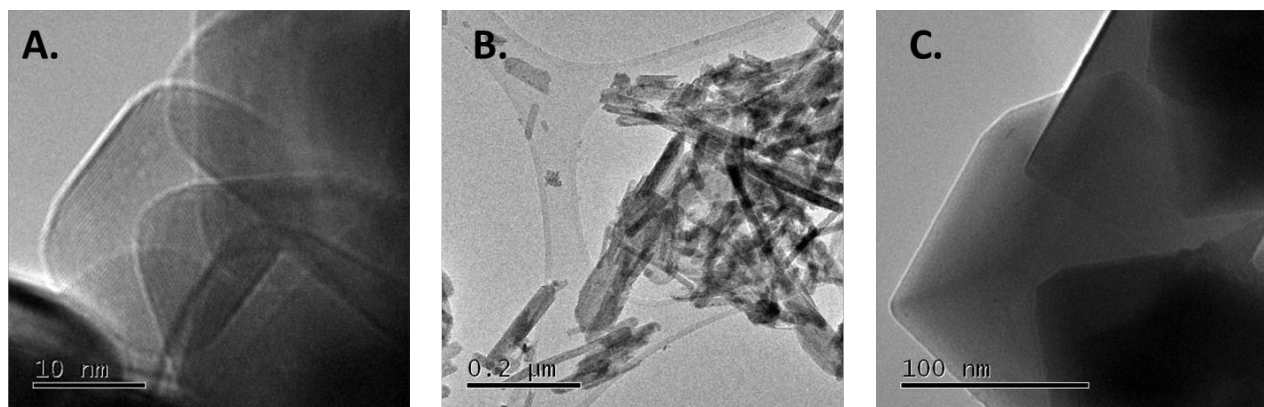


Figure 1: TEM pictures of the A. 20 wt.% Fe/Ceria nanoparticles, B. 20 wt.% Fe/Ceria nanorods and C. 20 wt.% Fe/Ceria nanocubes.

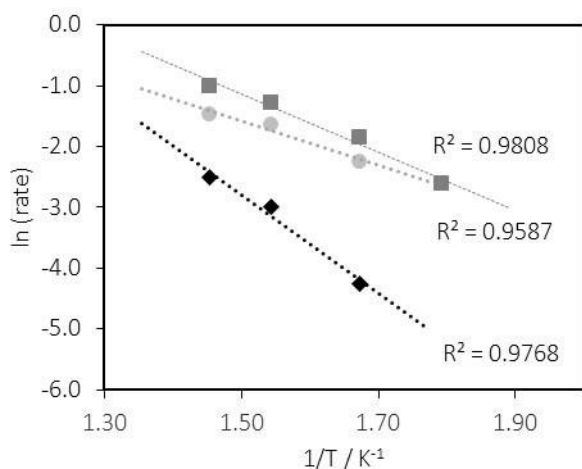


Figure 2: Arrhenius plot for the CO_2 hydrogenation reaction with \blacklozenge 20 wt.% Fe/CeO₂ particles \blacksquare 20 wt.% Fe/CeO₂ rods \bullet 20 wt.% Fe/CeO₂ cubes. Rate values are expressed as mol HC formed mol_{Fe}⁻¹ h⁻¹.

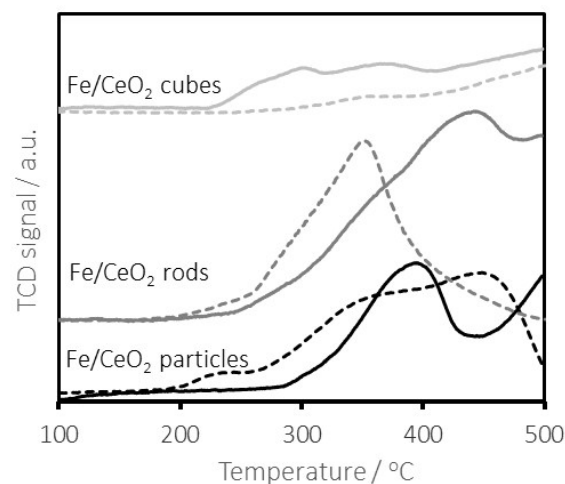


Figure 3: Temperature programme reduction of the different 20 wt.% Fe/ceria catalysts (solid line) and their corresponding ceria support (dashed line). Data is normalised per mass of catalyst.

In addition, similar methane selectivities (70-80 %) versus longer HC are observed in all the catalytic systems with the exception of the Fe/ceria particles that only produce methane at temperatures below 350 °C. Iron-only catalysts in the absence of promoters such as K, Mn, etc are known to produce CH₄ as main product²⁹ in a similar catalytic pathway that occurs during natural gas formation in coalbeds producing a natural gas composition with > 90% methane³⁰. In this study, we have intentionally avoided the addition of any modifier to understand the role of the morphology of nanostructured ceria support on the iron active species and their resulting reactivities.

As the reaction temperature increases, the HC selectivity of the Fe/ceria rods catalyst greatly increases up to 350 °C compared to the ceria cubes counterpart whose HC selectivity is almost independent on temperature. Indeed, the apparent activation energy of the Fe/ceria cubes is considerable lower (30.2 kJ mol⁻¹) than that of the Fe/ceria rods (44.6 kJ mol⁻¹) (Figure 2). On the other hand, Fe/ceria particles present a high activation energy (67.3 kJ mol⁻¹) with only formation of C₁-C₂ hydrocarbons suggesting that the growth-chain probability is greatly limited in this system.

The XRD spectra of the different Fe/CeO₂ catalysts show the crystalline structure of the support with diffraction patterns corresponding to the pure cubic phase (ceria fluorite structure, JCPDS 34-0394)²⁵. Additionally, diffraction peaks at 2 θ angles of 35.5° and 62.5° corresponding to the (110) and (214) planes of the Fe₂O₃ are also present. The former peak is used to calculate the Fe₂O₃ crystallite size using the Scherrer's equation showing a similar average iron size (~30 nm) when ceria rods and cubes are used as support. On the contrary, an iron average size of ~73 nm is present on the catalysts supported on ceria particles. The similarity of the iron species sizes in the rods and the cubes

catalysts and the difference in reactivity reveals the intrinsic effect of the morphology of the ceria support. In general, the olefin/paraffin ratio increases as the reaction temperature increases, however, olefin formation is greatly promoted when ceria particles and cubes are used as support in comparison to the ceria rods counterparts. Ceria rods are known to selectively expose the (110) and (100) surface planes, presenting a higher surface oxygen concentration and higher reducibility at lower temperatures than the ceria particles enclosing (111) and (100) facets and the ceria cubes with exposed (100) planes²⁵. Indeed, the ceria reducibility decreases in the order rods > particles > cubes, following the same trend that the olefin/paraffin ratio suggesting that the ceria support can play a key role on the saturation of the HC products, especially in the catalyst supported on the ceria rods. Although the catalysts are reduced at 400 °C prior the reaction, the support can also have an effect on the actual iron species formed under reaction conditions⁵ and the reduction degree of the iron due to the different concentration of surface oxygen species in the support. The temperature programme reduction of the different nanostructured ceria supports are shown in Figure 3, in addition to their corresponding Fe/ceria counterparts. The bare ceria nanoparticles and nanorods present a reduction peak starting at ~250°C related to the reduction of readily reduced ceria oxygen (in some cases also called surface oxygen) while the extension of this peak in the ceria nanocubes is comparably smaller. Indeed, we have recently shown that only 10% of the oxygen available in the ceria nanocubes is readily reducible oxygen compared to the 35 – 45% in the ceria nanoparticles and nanorods²⁶. Desauvay *et al.*³¹ have recently shown the contribution of the different crystal plane exposure to the low temperature reduction peak, formed by inter-convoluted peaks.

Table 2: Catalytic performance of 20 wt.% Fe-1 wt.% Pt supported on nanostructured ceria for the hydrogenation of CO₂

| Catalyst | Reaction temperature / °C | CO ₂ conversion / % | Selectivity CO / % | Selectivity to HCs / % | Hydrocarbon selectivity / % | | | | | Olefin/paraffin ratio |
|--|---------------------------|--------------------------------|--------------------|------------------------|-----------------------------|--------|------|-------|-----|-----------------------|
| | | | | | CH ₄ | C2-4 = | C2-4 | C5+ = | C5+ | |
| 20wt.% Fe / CeO ₂ rods + 1 wt.%Pt / CeO ₂ rods (physical mix) | 260 | 16.9 | 92.3 | 7.69 | 75.0 | 0.0 | 21.7 | 0.0 | 1.4 | 0.00 |
| | 300 | 19.8 | 88.9 | 11.1 | 74.9 | 0.0 | 24.1 | 0.0 | 0.3 | 0.00 |
| | 350 | 32 | 75.39 | 24.7 | 93.8 | 0.0 | 6.1 | 0.0 | 0.0 | 0.00 |
| | 390 | 48.6 | 61.9 | 38.1 | 99.4 | 0.0 | 0.6 | 0.0 | 0.0 | 0.00 |
| 20wt.% Fe / CeO ₂ cubes + 1 wt.%Pt / CeO ₂ cubes (physical mix) | 260 | 5.3 | 90.6 | 9.4 | 68.7 | 1.6 | 24.5 | 0.0 | 2.3 | 0.06 |
| | 300 | 11.5 | 87.0 | 13.0 | 60.7 | 2.8 | 34.3 | 0.0 | 0.6 | 0.08 |
| | 350 | 12.5 | 78.4 | 21.6 | 59.7 | 1.7 | 37.3 | 0.0 | 0.2 | 0.04 |
| | 390 | 15.2 | 73.0 | 27.0 | 78.6 | 0.6 | 19.7 | 0.0 | 1.0 | 0.03 |
| 20wt.% Fe / CeO ₂ cubes + 1 wt.%Pt / CeO ₂ cubes (co-impregnation) | 260 | 6.7 | 94.3 | 5.7 | 66.2 | 10.7 | 23.1 | 0.0 | 0.0 | 0.47 |
| | 300 | 5.5 | 70.9 | 29.1 | 57.5 | 11.1 | 26.0 | 1.2 | 1.2 | 0.45 |
| | 350 | 11.9 | 79.0 | 21.0 | 53.5 | 12.5 | 30.4 | 0.1 | 1.6 | 0.39 |
| | 390 | 16.3 | 85.9 | 14.1 | 62.2 | 7.3 | 29.0 | 0.4 | 1.1 | 0.25 |

Reaction conditions: 0.3 g of each catalysts (total of 0.6 g when physical mixtures are used) pre-reduced at 400°C under 50 mL min⁻¹ H₂ flow. Inlet gas: 8 mL min⁻¹ of 3:1 H₂/CO₂ ratio. GHSV: 200 h⁻¹

The experimental error associated to the analysis is < 4%.

The presence of iron, increases the reduction temperature in the catalysts supported on the ceria particles and rods in respect to the corresponding ceria support, suggesting a high metal-support interaction. Contrary, it appears that the Fe/CeO₂ cubes catalyst partially reduces at lower temperatures (<300 °C) than the particles and rods counterparts. Interestingly, the initial reduction temperature of the Fe/Ceria catalysts is directly related to the olefin/paraffin ratio observed in this system.

The addition of platinum in F-T catalysts has been demonstrated to facilitate the reduction of the active species, especially in cobalt-based catalysts³². In order to further facilitate the formation of the iron active species on the Fe/CeO₂ catalysts, the Fe/CeO₂ rods and the Fe/CeO₂ cubes catalysts were physically mixed with (1 wt.%)Pt/CeO₂ rods and Pt/CeO₂ cubes respectively. The CO₂ conversion greatly increases, Table 2, in the case of the ceria rod catalysts due to the high reactivity of the platinum species in the RWGS reaction under these conditions²⁴. However, the mixture of Fe/CeO₂ and Pt/CeO₂ rods catalysts produce only methane and CO as products (Table 2). In the case of the physical mixture of iron and platinum catalysts supported on ceria cubes, no obvious effect of the presence of platinum on the CO₂ conversion or HC selectivity is observed compared to the only-Fe catalyst. However, the ability of platinum particles to spill-over hydrogen on the ceria surface³³ greatly promotes the saturation of the HC products, leading to very low olefin/paraffin ratios. Additionally, when iron and platinum are co-impregnated on ceria cubes (Table 2), the CO₂ conversion and selectivity to HC are slightly lower than in the iron-only catalyst.

However, the methane selectivity versus longer HC is considerable lower in the presence of co-impregnated platinum. Although the olefin/paraffin ratio is higher in the co-impregnated catalysts than with a physical mixture of Fe and Pt ceria, the ratio is significantly lower than in the only-Fe/CeO₂ cubes catalysts, demonstrating that promotion of hydrogen spill-over can minimize the previously discussed effect of the support in the selectivity³⁴.

In conclusion, this study demonstrates that the morphology of the ceria support on Fe/CeO₂ catalyst plays a key role not only on the CO₂ conversion but also on the methane to hydrocarbon selectivity and the olefin to paraffin ratio. Iron supported on nanostructured ceria rods presents the highest hydrocarbon selectivity versus CO formation however higher olefin/paraffin ratios are achieved with ceria cubes as support. This modification of the iron reactivity is related to the high metal-support interaction shown by the shift of the reduction temperatures of the Fe/CeO₂ catalysts in respect to their corresponding supports, associated to the selective exposure of different crystal planes in the different ceria morphologies. Addition of either platinum/ceria catalysts or co-impregnation with iron, greatly promotes the saturation of the products masking the effect of the support.

Notes and references

‡ Nanostructured ceria was synthesised by an alkali hydrothermal method using an un-stirred acid digestion bomb equipped with a PTFE liner using the conditions described in the text. Further details can be found elsewhere²⁵. Iron and platinum was supported on the different

supports via incipient wetness impregnation using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and H_2PtCl_6 as iron and platinum precursors respectively. X-ray diffraction (XRD) characterisation was carried out using an X'Pert PRO diffractometer by PANalytical with a $\text{Cu K}\alpha$ radiation and the crystalline phases were identified by matching the experimental patterns to the JCPDS powder diffraction file database. Temperature programmed reductions (TPR) were carried out under a 50 mL min^{-1} 5% H_2/Ar flow from room temperature to 500°C with a heating rate of $10^\circ\text{C min}^{-1}$. The activity of the catalysts in the direct CO_2 hydrogenation reactions was measured using a differential packed bed reactor where the catalysts were in-situ pre-reduced at 400°C under 50 mL min^{-1} H_2 flow. In a typical experiment, 0.3 g of the catalyst was diluted in SiC up to a 2.5 cm^3 catalytic bed. The test were carried out at atmospheric temperature using 8 mL min^{-1} H_2/CO_2 feed with 3:1 volumetric ratio. The outlet gas was analysed by gas chromatography (Agilent 7890A) fitted with a FID, TCD and a Mass Spec. The experimental error associated to the analysis is $< 4\%$.

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