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Manufacture of highly loaded silica-supported cobalt Fischer–Tropsch catalysts from a metal organic framework

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The development of synthetic protocols for the preparation of highly loaded metal nanoparticle-supported catalysts has received a great deal of attention over the last few decades. Independently controlling metal loading, nanoparticle size, distribution, and accessibility has proven challenging because of the clear interdependence between these crucial performance parameters. Here we present a stepwise methodology that, making use of a cobalt-containing metal organic framework as hard template (ZIF-67), allows addressing this long-standing challenge. Condensation of silica in the Co-metal organic framework pore space followed by pyrolysis and subsequent calcination of these composites renders highly loaded cobalt nanocomposites (~50 wt.% Co), with cobalt oxide reducibility in the order of 80% and a good particle dispersion, that exhibit high activity, C5 + selectivity and stability in Fischer–Tropsch synthesis.
Metal (oxide) nanoparticles are instrumental in the development of new applications: from the production of fuels and chemicals through catalytic processes to nanoelectronics and energy conversion and storage. Because most chemical and electronic phenomena occur at the surface, the intrinsic properties of nanoparticles depend strongly on their size, spatial distribution and even on their shape. In general, small nanoparticles show high surface energies and are thermally unstable and prone to aggregate into larger clusters. To tackle this issue, a general strategy consists of the use of supports with high surface area and well-developed porosity (e.g., SiO2 and Al2O3) that stabilize and prevent nanoparticle aggregation.

Structure sensitive reactions such as Fischer–Tropsch synthesis (FTS) are an outstanding example. For this specific process, when Co is used as the active metal, catalytic activity and selectivity to long-chain hydrocarbons are maximized when nanoparticles in the order of 8–30 nm are used. Because of this reason, impregnation is the most widely used method for the preparation of supported nanoparticles. Metal loading, nanoparticle size, and distribution are the three most important parameters that define performance of supported nanoparticles. Although it would be ideal to control independently each one of these parameters, in reality a strong interdependence exists. For example, for the methods described above, metal loading and particle size usually go hand in hand as a result of the fact that bigger nanoparticles and/or clusters are formed when high metal loadings are used. This interdependence is a clear drawback for the development of more efficient nanoparticle based composites for application in, i.e., heterogeneous catalysis.

Results

Catalyst synthesis and characterization. Figure 1 illustrates the followed synthetic procedure. We used the zeolitic imidazolate-framework ZIF-67, containing a 30 wt.% Co (Co(MeIm)2, MeIm = 2-methylimidazolate) and tetramethyl orthosilicate (TMOS) as starting materials for the synthesis of cobalt catalysts. In this approach, a TMOS impregnated ZIF-67 was first subjected to a wet N2 flow under ambient conditions to facilitate TMOS hydrolysis inside the pores of the MOF. The obtained ZIF-67@SiO2 sample was then pyrolyzed at different temperatures in the range of 773–973 K under N2 for 4 h, followed by calcination in air at 673 K for 2 h. The catalysts after pyrolysis and calcination are denoted as Co@C-SiO2-T and Co@SiO2-T, respectively, with
Fig. 2 Electron microscopy images and corresponding nanoparticle size distributions of cobalt based samples. a High-angle annular dark-field scanning electron (HAADF-STEM) micrograph of ZIF-67@SiO₂ (scale bar 200 nm). Elemental mapping of b Si, c Co, and d C in ZIF-67@SiO₂ sample (scale bars 200 nm). TEM micrograph of e Co@SiO₂-cal, f Co@SiO₂-773 with an inset of the observable needle-like structure, g Co@SiO₂-873 and h Co@SiO₂-973 (scale bars from (e) - (h) 50 nm). Particle size histograms obtained from TEM analysis for i Co@SiO₂-cal, j Co@SiO₂-773, k Co@SiO₂-873, and l Co@SiO₂-973. Electron tomography results for m, n, o Co@SiO₂-cal (scale bar 50, 50, and 100 nm, respectively), and p, q, r Co@SiO₂-873 (scale bar 50, 50, and 100 nm, respectively)
The pyrolysis temperature. For comparison, a Co@SiO2-catalyst sample was also prepared by direct calcination (skipping the intermediate pyrolysis step) of ZIF-67@SiO2 in air (details of the preparation process for all materials are shown in the Methods section). The Co loadings of the Co@SiO2 catalysts are ~50 wt.% (Supplementary Table 1).

The X-ray diffraction (XRD) pattern of the original ZIF-67 (Supplementary Fig. 1), confirms the structure of the MOF precursor30. Thermogravimetric (TG) analysis in N2 atmosphere of the hydrolyzed ZIF-67@SiO2 indicates that the complete pyrolytic decomposition of the crystalline ZIF-67 occurs in the range of 800–850 K (Supplementary Fig. 2), further confirmed by XRD (Supplementary Fig. 3a). After the pyrolysis step, graphite (20 = 30.6°) and metallic cobalt (20 = 51.8°, 60.6°) phases are formed. Notably, when a higher pyrolysis temperature is used, these peaks become much narrower and sharper, indicating a higher graphitization degree and a larger crystallite size of cobalt nanoparticles31. After the additional calcination step, the characteristic peaks corresponding to ZIF-67, graphite, and Co@SiO2 catalysts are observed (Supplementary Table 1).

Both ZIF-67 and ZIF-67@SiO2 display type-I N2 sorption isotherm (Supplementary Fig. 4a) typically associated with microporosity32. The Brunauer-Emmett-Teller area (S BET) and pore volume (V p) decreases from 1930 m2 g−1 and 0.71 cm3 g−1 to 1430 m2 g−1 and 0.56 cm3 g−1 after incorporation of SiO2 (Supplementary Table 1)33. In contrast with the original ZIF-67@SiO2, the S BET and V p of all Co@SiO2 catalysts decreases drastically and exhibit type IV isotherms with type H3 hysteresis that closes at P/P0 ≈ 0.4, suggesting the presence of a predominantly mesoporous structure which is the result of the agglomerated small SiO2 particles (Supplementary Fig. 3b).

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) analysis in combination with elemental mapping (STEM/EDX (elemental energy dispersive X-ray)) give further information on the textural properties of the composites at different synthesis stages. High-angle annular dark-field scanning electron (HAADF-STEM) (Fig. 2a) analysis shows a well-defined rhombic dodecahedral morphology (~250 nm) of the ZIF-67@SiO2 catalysts similar to that of the original ZIF-6730, whereas elemental mapping demonstrates an homogeneous dispersion of Si, Co and C (Fig. 2b–d). After pyrolysis under N2 atmosphere, well-dispersed cobalt nanoparticles in the carbon matrix can be observed in Co@C-SiO2-T samples (Supplementary Fig. 5a–c), with average particle size increasing from 5.4 nm in Co@C-SiO2-773 to 11.0 nm in Co@C-SiO2-873, and 13.3 nm in Co@C-SiO2-973 (Supplementary Fig. 5d–f). According to HR-TEM, during pyrolysis, cobalt nanoparticles are encapsulated by multilayers of graphitic-carbon shells (Supplementary Fig. 5g–i) that render them, most likely, inaccessible. XRD analysis further confirm this observation, since reoxidation of most Co does not occur upon exposure to atmospheric conditions (vide supra). In addition, leaching experiment using HCl demonstrates that only a 30% of cobalt can be leached (Supplementary Table 2). The subsequent calcination removes the graphite shells and oxidizes metallic cobalt to Co3O4 (Fig. 3f–h, and Supplementary Fig. 6b–d), but hardly affects Co-particulate size (Fig. 3j–l, and Table 1). No large cobalt clusters can be found in the Co@SiO2-773 sample even after reduction in H2 at 673 K for 10 h (Supplementary Fig. 7a–d). Interestingly, Co@SiO2-catalyst (Fig. 2e, m and Supplementary Fig. 8a) and Co@SiO2-773 (the inset of Fig. 2f) show the presence of needle-like structures absent in samples pyrolyzed at higher temperatures. Additional analysis by combining TEM and EDX (Supplementary Fig. 8b, c) reveals the presence of both Si and Co in needle-like areas and made us tentatively attribute this morphology to the formation of cobalt phyllosilicates34.

The reducibility of the metallic species in all calcined samples was studied by temperature-programmed reduction in H2 (TPR (H2)). All of the Co@SiO2 samples exhibit two overlapping reduction peaks centered at ~570 K and 700 K, and a broad reduction band between 850 and 1150 K, as shown in Fig. 3. The first two peaks are ascribed to the two-step reduction of Co3O4 (Fig. 2f–h, and Supplementary Fig. 6b–d), but hardly affects Co-particulate size (Fig. 3j–l, and Table 1). No large cobalt clusters can be found in the Co@SiO2-773 sample even after reduction in H2 at 673 K for 10 h (Supplementary Fig. 7a–d). Interestingly, Co@SiO2-catalyst (Fig. 2e, m and Supplementary Fig. 8a) and Co@SiO2-773 (the inset of Fig. 2f) show the presence of needle-like structures absent in samples pyrolyzed at higher temperatures. Additional analysis by combining TEM and EDX (Supplementary Fig. 8b, c) reveals the presence of both Si and Co in needle-like areas and made us tentatively attribute this morphology to the formation of cobalt phyllosilicates34.

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### Table 1: Average cobalt particle size and DOR of Co@SiO2 catalysts

| Samples     | dCo,a    | dCo,b    | DOR (%) |
|-------------|----------|----------|---------|
| Co@SiO2-773 | 8.6      | 7.6      | 66      |
| Co@SiO2-873 | 12.3     | 11.8     | 78      |
| Co@SiO2-973 | 14.3     | 13.5     | 79      |
| Co@SiO2-cal.| 10.7     | 9.5      | 52      |

| a Cobalt particle size is obtained from TEM analysis using at least 200 Co3O4 nanoparticles and calculated from CoO particle size using Co and CoO densities. | b Cobalt particle size is calculated from H2-chemisorption assuming the surface stoichiometry H/Co = 1 and an atomic cross-sectional area of 0.0662 nm2. Cobalt oxide degree of reduction (DOR). |
Catalytic results. The Co@SiO₂ catalysts were tested in the FTS at 483 K, 20 bar, H₂/CO = 1, and a space velocity of 0.5 mol CO g⁻¹ cat. h⁻¹. Figure 4a shows time-on-stream (TOS) evolution of CO conversion. All catalysts exhibit a good stability, and differences observed in activity are in line with the observed textural properties. Co@SiO₂-873 displays the highest CO conversion, followed by Co@SiO₂-773 and Co@SiO₂-973. Table 2 summarizes cobalt-time-yield (CTY), apparent turnover frequencies (TOF) and product selectivity for these catalysts after 102 h on stream. When CTY is plotted as a function of the pyrolysis temperature, a volcano-like curve is obtained, with an optimum for the sample Co@SiO₂-773 (Fig. 4b). The FTS process occurs on the surface of metallic cobalt nanoparticles with an optimal particle size around 10 nm. On one hand, small cobalt nanoparticles normally possess a large fraction of low-coordinated surface sites (i.e., corner, kink, edge etc.), which to a large extent hamper CO dissociation and/or CH₄ hydrogenation. Hence, we attribute the superior activity of Co@SiO₂-873 to the high Co reducibility and the optimal Co-particle size (Table 1). On the other hand, small cobalt nanoparticles have only few step sites, known for C-C formation towards long chain hydrocarbons, therefore resulting in a high methane selectivity. Thus, the larger Co-particle size in the Co@SiO₂-873 and Co@SiO₂-973 samples when compared to Co@SiO₂-773 results in a lower CH₄ and a higher C₅+ selectivity for these catalysts (Table 2), in excellent agreement with literature. We argue that the low H₂/CO ratio and operating temperature applied in this work (H₂/CO = 1, 483 K) along with an optimal cobalt particle size in the synthesized Co@SiO₂-873 catalyst result in a chain growth probability (α) as high as 0.94. The performance of the Co@SiO₂-cal. sample further emphasizes the key role of the intermediate pyrolysis step (Table 2). A high initial CO conversion over this sample along with a clear deactivation during the first 50 h on stream (Supplementary Fig. 10) is observed. We attribute the severe deactivation at the initial stage to the presence of a substantial amount of small cobalt nanoparticles (<4 nm), that are more susceptible to aggregation and/or oxidation than larger particles during high-pressure FTS and which also more selective for the formation of CH₄. In addition, although pyrolysis of Co-based MOFs under an inert atmosphere has recently been demonstrated as a promising route to prepare highly loaded Co@C hybrids with controllable cobalt particle size and distribution, these directly pyrolyzed samples such as Co@C-873 and Co@C-SiO₂-873 synthesized in this work show a poor activity and low C₅+ selectivity along with an unacceptable CH₄ selectivity in the FTS process under the same conditions as Co@SiO₂ catalysts (Supplementary Fig. 11 and Supplementary Table 3). The inferior performance of these pyrolyzed samples can be ascribed to the inaccessibility of most cobalt nanoparticles, which are completely encapsulated by graphitic shells. (Supplementary Fig. 12 and Supplementary Table 2) Comparison of our results demonstrates the importance of the synthetic protocol here presented.

Discussion

The results here presented demonstrate that the stepwise hydrolysis-pyrolysis-calcination methodology is a promising route to synthesize highly loaded Co@SiO₂ catalysts using ZIF-67 as a sacrificial template and TMOS as silicon source. During the high-temperature pyrolysis, the ZIF-67 structure decomposes, generating cobalt nanoparticles encapsulated by graphitic-carbon shells, which prevent the formation of large agglomerates, controlling in this way cobalt particle dispersity, whereas optimization of the pyrolysis temperature improves cobalt reducibility.
To further demonstrate the advantages of this synthetic methodology, we prepared additional highly loaded Co catalysts, with Co supported on commercially available Aerosil-200 (denoted as A) or CARiACT Q-10 (denoted as F) silica, by using melt infiltration (MI). Also two benchmark Co/SiO2 catalysts with cobalt loading of 16 wt.% and 32 wt.%, respectively, were prepared by means of incipient wetness impregnation (IWI). The 32 wt.%Co/SiO2-F-TIWI and 40 wt.%Co/SiO2-A-MI catalysts consist mostly of large aggregates (Supplementary Fig. 13a–c, and Supplementary Fig. 14a, b) as a result of the lower versatility of the MI and IWI methods for high cobalt loadings. The comparison between the FTS performance of these catalysts and Co@SiO2-873 is shown in Fig. 5a, b and Table 3. Under the studied conditions, the Co@SiO2-873 displays a CTY at least 1.5 times (H2/CO = 1) (entry 1–4, Table 3) and/or 2.2 times (H2/CO = 2) (entry 5 and 7, Table 3) higher than the other samples (in spite of the higher Co loading) and a comparable C5 + selectivity (~83%) to its Co/SiO2-F-TIWI counterpart at a similar CO conversion level (~26%). Interestingly, TEM images of the Co@SiO2-873 catalyst after 201 h TOS show a very good dispersion of cobalt nanoparticles on the SiO2 support along with very few aggregates (Supplementary Fig. 15a–d), in good agreement with the observed very mild catalyst deactivation with time-on-stream. In comparison with other highly loaded catalysts prepared using traditional methods, the optimal particle size and high stability of cobalt nanoparticles in Co@SiO2-873 lead to more available cobalt sites and explain the high activity of Co@SiO2-873 in the FTS process.

Overall, our results further highlight the potential and versatility of the use of MOFs as catalyst templates and opens the door to the controlled fabrication of highly loaded, accessible, active and stable metal supported catalysts thus coping with a major challenge in materials science and industrial catalysis.

### Methods

#### Synthesis of the parent ZIF-67

In the synthesis of ZIF-67, 2.933 g of Co(NO3)2·6H2O and 6.489 g of 2-methylimidazole (Melm) were separately dissolved in 200 ml methanol. The latter clear solution was rapidly poured into the former pink solution with vigorous stirring for 24 h at room temperature. Afterwards, the bright purple products were collected by filtration, washed with methanol, and dried at 353 K for 10 h under vacuum.

#### Synthesis of ZIF-67@SiO2

A total of 0.8 g of the synthesized ZIF-67 was immersed in 5 ml TMOS in an autoclave, which was further transferred into a rotation oven and heated up to 333 K overnight. After the oven was cooled down to room temperature, the mixture was carefully washed with 1 ml ethanol to remove the excess TMOS on the external surface of ZIF-67 by filtration. Then the purple material was placed in a cotton thimble of 22 mm diameter and placed in a glass tube of 22 mm diameter. The glass tube was fitted to a round bottom flask containing 500 ml of water. A needle to bubble the water with 10 ml min⁻¹ of N2 flux was also fitted. The temperature was raised to 323 K to create a wet N2 stream to directly hydrolyze the TMOS molecules for 30 h, followed by air drying at 333 K and vacuum drying at 373 K for 10 h, successively. The obtained sample was denoted as ZIF-67@SiO2.

#### Synthesis of Co@C-SiO2-T

A total of 0.8 g of ZIF-67@SiO2 were transferred into a quartz tubular reactor (I.D. = 5.0 cm) horizontally situated in a ceramic fiber oven (Carbolite, Sheffield). The reactor was flushed with N2 at 303 K for 0.5 h, followed by direct carbonization at different temperature for 4 h under N2.
(150 ml min⁻¹) at a ramp of 2 K min⁻¹. The obtained sample was denoted as Co/C-SiO₂-T, where T (T=773, 873, 973 K) refers to the pyrolysis temperature.

**Synthesis of Co/SiO₂-T and Co/SiO₂-C.** The obtained Co/C-SiO₂-T samples were further calcined at 673 K in air (150 ml min⁻¹) for 2 h at a ramp of 1 K min⁻¹, and denoted as Co/SiO₂-T₉. The obtained Co/SiO₂-C sample, where T (T=773, 873, 973 K) refers to the pyrolysis temperature. For comparison, 0.8 g of ZIF-67/SiO₂ was directly calcined at 673 K in air (150 ml min⁻¹) for 2 h at a ramp of 1 K min⁻¹, and this sample was denoted as Co/SiO₂-Cal.

**Synthesis of Co/C-SiO₂.** Co/C-SiO₂ was prepared by pyrolysis of 0.8 g ZIF-67 at 873 K for 4 h under 150 ml min⁻¹ N₂ flow at a ramp of 2 K min⁻¹.

**Synthesis of Co/SiO₂ catalysts with conventional methods.** For the MI samples, 2.9 g Co(NO₃)₂·6H₂O and 0.6 g of degassed SiO₂ support (Aerosil-200 or Cargill SiO₂) were physically mixed in a mortar with a pestle under ambient conditions until the powder was homogeneously pink. Then the samples were transferred into a Teflon-lined steel autoclave and kept at 333 K for 24 h, followed by calcination by heating to 673 K (1 K min⁻¹, 2 h) in a flow of air (150 ml min⁻¹) for 8 h (No weight loss was obtained after this time). After that the temperature was increased to 1223 K. The DOR was measured using TGA (Mettler Toledo TGA/SDTA 851e) in a flow of 10% H₂/He. The samples were heated to 673 K and held there for 8 h (No weight loss was obtained after this time). After that the temperature was further increased to 1273 K (5 K min⁻¹). The DOR of cobalt was calculated using the equation (2)

$$\frac{\frac{d_m}{d_{m1}}}{\frac{\alpha_{SiO₂}}{\alpha_{SiO₂}} - \frac{\alpha_{CoS} - 1}{\alpha_{CoS} - 1}}$$ (2)

where \( n \) is the number of particles with diameter of \( d \). The bright-field and HAADF STEM imaging of the Co/SiO₂-F-TIW sample was performed using a JEOL JEM-2010 microscope at 200 kV. Tilt series were aligned and reconstructed using IMOD software package. Cobalt particle diameter (\( d_{Co} \)) was calculated based on a minimum of 200 nanoparticles using the equation (1)

$$d_{Co} = \sqrt{\frac{n}{m d_{m1}} \sum n d_{1}^2 - \sum n d_{1}^2}$$ (1)

A Micromeritics ASAP 2020 was used to measure H₂ chemisorption. Samples dried at 100 °C were submitted to reduction in H₂ at 673 K (10 h, 5 K min⁻¹) and evacuation at the same temperature. Isotherms were measured at 423 K. Temperature-programmed reduction in hydrogen (TPR(H₂)) was performed in a parallel flow of 10 vol.% H₂/Ar (30 ml min⁻¹) at a heating rate of 5 K min⁻¹ from ambient temperature to 1223 K. The DOR was measured using TGA (Mettler Toledo TGA/SDTA 851e) in a flow of 10% H₂/He. The samples were heated to 673 K and held there for 8 h (No weight loss was obtained after this time). After that the temperature was further increased to 1273 K (5 K min⁻¹). The DOR of cobalt was calculated using the equation (2)

$$\frac{\frac{d_m}{d_{m1}}}{\frac{\alpha_{SiO₂}}{\alpha_{SiO₂}} - \frac{\alpha_{CoS} - 1}{\alpha_{CoS} - 1}}$$ (2)

**Catalytic testing.** The FTS was carried out in a parallel 6-flow fixed-bed micro-reactor setup as previously described. Certain amount of catalyst was mixed with SiC of similar size and loaded into a stainless steel tube lined with a quartz layer. Catalysts were reduced in situ in pure H₂ at 673 K for 10 h at 2 K min⁻¹. Afterwards, the reactors were cooled to 453 K at which the pressure was increased to the target pressure (20 or 26 bar) under H₂. Then, a CO flow was gradually introduced into the system, and finally reached an H₂/CO ratio of 1 or 2 with syngas flow of 10 ml min⁻¹. Next, the temperature was increased to the reaction temperature of 483 K at 2 K min⁻¹. The C5 + selectivity was calculated from the CO conversion by subtracting the fraction of CO used for the formation of C₅ to C₆ products, as determined via online GC (Hewlett Packard 5890, Series II) using N₂ as an internal standard, from the total amount of converted CO.

**Data availability.** The authors declare that all other relevant data not included in the Supplementary Information and supporting the findings of this study are available on request.

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Author contributions
X.S. and J.G. conceived, coordinated the research and designed the experiments. X.S. and A.I.O.S. synthesized and characterized the catalysts. X.S. performed most of the catalytic experimentation and extensive product evaluation. Rev. Sci. Instrum. 84, 124101 (2013).

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