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Recent developments in the application of nanomaterials to understanding molecular level processes in cobalt catalysed Fischer-Tropsch synthesis

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This perspective offers an overview of using nanomaterials for understanding cobalt catalysed Fischer-Tropsch chemistry. Nanomaterials now afford unprecedented control of size, shape and structure at the nanometre scale. This makes them invaluable tools for studying heterogeneous catalysis. The Fischer-Tropsch reaction, especially using cobalt based catalysts, is a linchpin in many processes for utilising other feedstocks (*via* gasification) that have been envisaged as short/medium term replacements for crude oil. The underlying chemistry has therefore garnered considerable renewed interest. The current state of the art in mechanistic understanding is summarised and the application of nanomaterials to developing this further is explored. Several specific questions, to which nanomaterials have already contributed answers, are addressed: how do nanomaterials contribute to our understanding of cobalt particle size effects, reducibility, and the effect of support porosity and how do precious metal promotors operate in cobalt catalysed Fischer-Tropsch chemistry? Future possible uses for nanomaterials in studying this field are also identified.

1. Introduction

The conversion of syngas (CO and H_2) to liquid hydrocarbons for use as fuels (and/or chemicals), known as Fischer-Tropsch (FT) synthesis (Figure 1), is a well-known, commercially utilised, and extensively studied heterogeneous catalytic reaction.

$$CO + H_2 \longrightarrow CxHy\text{ (alkanes/alkenes)} + H_2O \left(+ CO_2 + \text{alcohols} \right)$$

Figure 1. General scheme for FT synthesis reaction from syngas to a range of potential products.

Despite its discovery in the early 20th century and intermittent commercial use since this time,[1,2] the last decade has seen a renewed interest in understanding and developing Fischer-Tropsch technology – for instance 50% of publications on 'Fischer-Tropsch' originate from only the last decade.[3] Moreover, in addition to new large scale production facilities in Malaysia and Qatar, producing tens of thousands of barrels per day, new pilot projects and research programs have been conducted by almost all major oil companies.[4] This growing importance of FT chemistry is primarily driven by the fact that transformation of coal, natural gas (or even biomass) into syngas and subsequent conversion by FT into liquid hydrocarbons offers a convenient route to 'drop in' replacement transportation fuels. Not only is this route not reliant on increasingly expensive crude oil reserves, but, unlike blue skies technologies, FT has a proven track record of commercial feasibility. This approach also does not rely on the conversion or adaptation of distribution systems and vehicle fleets. Additionally, although the specifics of the process, including the catalyst, would ideally be designed around a specified feedstock,[5] the process is in principle adaptable to a wide range of feedstocks – including 'green' bio-feedstocks. Since liquid fuels can be transported by ship, Fischer-Tropsch technology (alongside liquefied natural gas) also provides a more secure alternative to pipelines in less politically stable regions of the world, where natural gas reserves exist.[4] It can, therefore, be expected to be a prevalent part of a medium-term solution to global energy challenges.

Typical catalysts for FT synthesis contain iron or cobalt (or in the research laboratory Ru) supported on a metal oxide support (*e.g.* alumina).[6,7] However, from their early development they have consisted of numerous promoters and additives (for instance the first BASF patent contained "cerium, cobalt, molybdenum or their alkali metallic oxides).[8] A typical catalyst is often a combination of half a dozen or more elements.[9] By way of example, screening conducted in development of the Co/Al_2O_3 catalyst for BP's Alaska pilot plant included Ru, Cr, Zr, Ga or La as promoters.[10] Although historically iron based

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catalysts were widely used, recently there has been a shift to cobalt based catalysts. This preference results from a combination of enhanced activity, higher chain growth probability and lower water gas shift activity with cobalt as the catalyst.[11] The former is important in achieving improved thermal efficiency while the latter two afford higher carbon efficiency, *i.e.* less of the carbon in the feedstock is wasted by being converted to CO_2, CH_4 and small (less desirable) hydrocarbon products. This has become increasingly important in the move to natural gas feedstocks over coal and with the increasing price of any carbon containing feedstock making carbon efficiency a key figure of merit. In addition, higher molecular weight products are more acceptable if aiming to make a range of products including diesel and chemicals, not just gasoline, as was often targeted in Fe catalysed processes.[12] The greater cost of Co over Fe also means there is a greater commercial desire to enhance and optimise the catalyst / avoid catalyst deactivation.

While the general aspects of Co catalysis in FT reactions are well reviewed elsewhere,[9,13] despite much research, the molecular surface mechanism appears to still remain less well understood. Improved knowledge of catalysts at this molecular and atomic level is essential for the rational development of improved (more energy efficient, selective, feedstock tolerant) catalysts. In this area much is to be learnt from the adaptation of nano-materials as *model catalysts*. The use of nanotechnology to develop advanced materials for use as model catalysts has been a key recent development in studying heterogeneous catalysis.[14,15,16,17] The advantage gained is that numerous model structures with good control over metal particle size, shape, composition and metal oxide structure and porosity can be made.[18] The uniformity that can be obtained is invaluable in two ways. Firstly, for catalytic tests it allows discrimination between different proposed active sites (if the different possibilities are dominant in different samples). Secondly, in spectroscopy, this uniformity means spectra do not originate from a huge range of different surface structures from different parts of the sample material, where only a small fraction of these are even at the catalytic site. Such simplification for elucidating spectroscopic problems has historically been achieved through the use of single crystal surfaces cleaned either electrochemically or in ultra-high vacuum. Studies performed on single crystal surfaces have provided many valuable insights, including in Fischer-Tropsch,[11,19] however there are also many aspects of these processes that require more complex structures to elucidate the coupled processes occurring on practical catalysts. As illustrated in Figure 2, the nanomaterials approach is a *next generation model* that enables us to advance our fundamental understanding of these situations where other effects are important. Such effects include particle size, or interaction of the metal or reactants with the oxide support. Nanomaterial

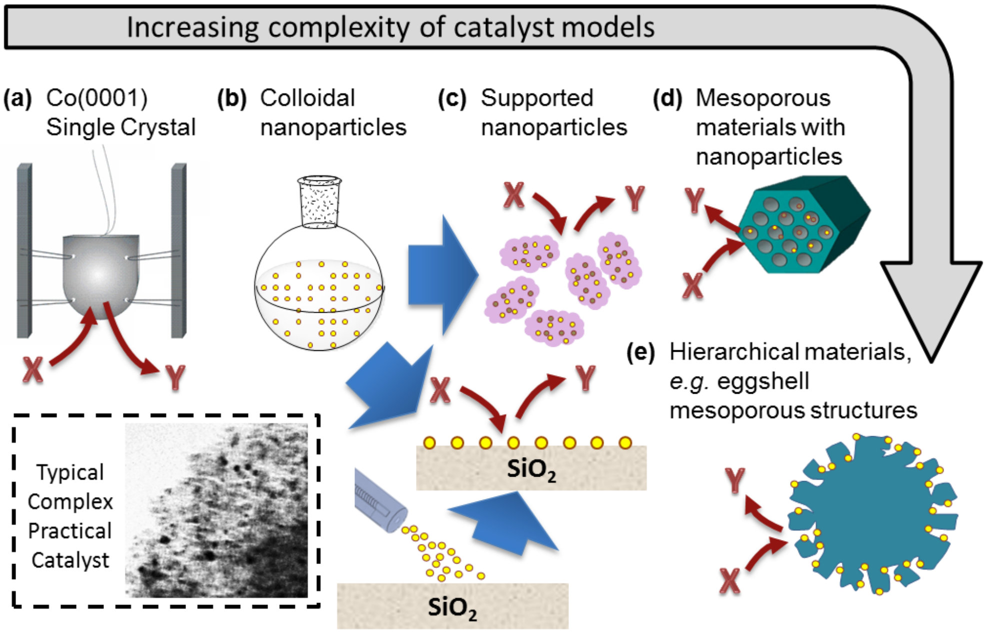

Figure 2. Schematic evolution of model catalysts in trend of increasing complexity, catalysing X → Y reaction: (a) single crystal metal sample; (b) colloidally prepared nanoparticles in solution (e.g. polyol method); (c) nanoparticles from b supported on metal oxide (top) or cast onto a 2-D substrate (bottom) – either as nanoparticles from solution (bottom-up control) or by deposition and growth / lithography (top-down control); (d) nanoparticles within well-defined mesoporous materials (obtained either by restricted growth within the mesopores or *via* capillary inclusion of nanoparticles obtained separately); and (e) hierarchical materials such as eggshell catalysts (discussed in the text), where ordered structures exist at several length scales. Inset shows a transmission electron micrograph of a typical 'complex' practical catalyst, prepared by incipient wetness impregnation, for comparison.

model catalysts have generally been generated in two modes as shown – some based on atomic and molecular deposition on well-defined substrates[16] and others using colloidal wet chemistry to generate well defined structures that can be built 'bottom up' into the desired catalyst structure.[18] Careful design of the oxide support can even be used to produce hierarchical structures with control at different lengthscales. This article gives a perspective of how catalysts containing well defined metal nanoparticles or nanostructured catalyst supports (or both) can be useful in better understanding mechanistic aspects of cobalt catalysed Fischer-Tropsch chemistry.

2. Molecular level understanding of FT catalysis on cobalt.

A great deal of work has been devoted to understanding the chemistry and kinetics of FT reactions, and specifically their impact on the product distribution obtained, as indicated in a number of reviews.[9,20,21,22] There is general agreement that CO is converted to a surface bound 'C1 monomer.' This monomer then undergoes polymerisation at the surface to form long chain hydrocarbons. The kinetics of the polymerisation are controlled by a balance of C1 addition (propagation) versus chain termination. The kinetics that result are therefore very similar to the Shultz-Flory like behaviour in condensation polymerisation, which, as identified by Anderson and others, is what gives rise to the overarching product distribution (now usually known as the Anderson-Schultz-Flory distribution).[23,24] Excess methane is often produced and various ratios of alkene/alkane may be obtained. It is known that reactant residence time in the catalyst increases the probability of readsorbing α-olefins that undergo further reaction; this reduces the alkene/alkane ratio for shorter hydrocarbons.[6] The latter observation has been demonstrated by co-feeding ethylene alongside the reactants, which adsorbs and reacts to form longer chains.[25] For pelleted catalysts diffusion rates can also impact heavily on the kinetics by becoming a reaction rate limiting factor,[26] although egg-shell type pellets, where the cobalt is only in the outer (egg) shell of the material, have been suggested as a way to deal with this in practical catalysts.[6]

The relatively well understood chain growth process, although important for selectivity, is not regarded as being a rate determining step. The arrival at surface 'C1 monomers' is much less straightforward. Indeed, as pointed out by Jager and Espinoza, there are many and varied kinetic expressions for the overall reaction that seem valid depending on the preparation method of the catalyst and the operation conditions.[9] Similarly, Ribeiro *et al*. identify that, although single studies identify the reaction to be structure insensitive (*i.e.* have a fixed TOF per cobalt surface site), preparation method of the catalysts, and especially support effects, are important in controlling the catalyst behaviour. Their attempts to use a single power law type kinetic expression to fit data from only 12 different studies still produced a difference in corrected turnover frequencies of a factor of 20.[27] (Rate = $kP_{H2}^{(0.7)}P_{CO}^{(-0.2)}$ was found to give the best fit.)

A particularly controversial area, which has been the subject of recent work by a number of leading groups, is whether CO dissociates directly (the *carbide mechanism*) or is first hydrogenated to a hydrogen containing intermediate following adsorption (the *indirect mechanism*), Figure 3.

It is known that in vacuum experiments at low pressure CO cannot dissociate on Co(0001) single crystal surfaces. However, non-basal planes containing step and kink sites are able to dissociate some of the CO molecules adsorbed on them.[11,19] CO can also be readily dissociated by cobalt foils (which contain many differently oriented crystallographic facets). However, experiments on these foils in vacuum showed the hydrogenation and removal of surface oxide rather than the dissociation of CO was the rate limiting step. [25]

For a long time the prevailing view has been that CO dissociation was the energetically hardest step in the production of the products and although other potential routes were mentioned, they were largely discounted, for example formyl and alcohol intermediates were already being discussed and discounted several decades ago.[21]

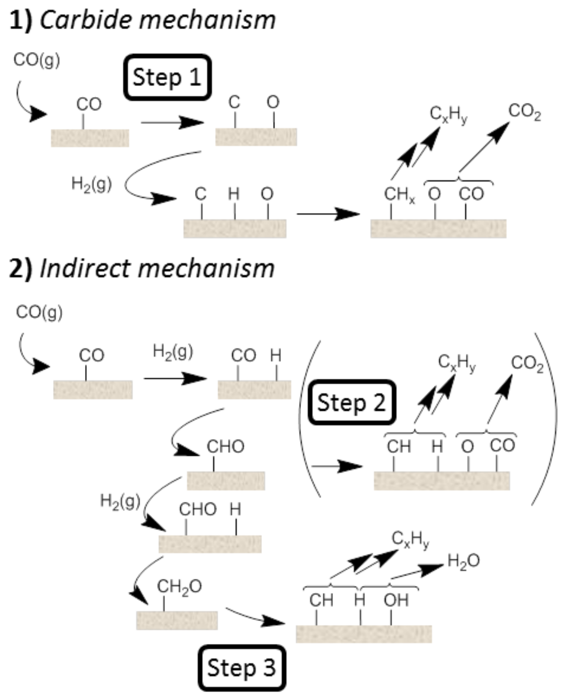

Figure 3. Reaction schemes for (1) *carbide* and (2) *indirect* mechanisms, *via* direct CO dissociation to form surface carbon (Step 1), or hydrogenation followed by subsequent dissociation (Step 2 or 3), respectively. Note: Schemes show only initial steps in the mechanism, the subsequent surface polymersiation to form C_xH_y species has been condensed for clarity. Also note the fate of oxygen as CO_2 or H_2O has been given as argued by reference 31 based on the dominance of CO_{ads} over H_{ads} on the catalyst surface and the independence of CO_2 production from H_2 partial pressure.

In 2008, Inderwildi *et al.* conducted DFT calculations of the reaction on a Co(0001) surface. They compared three steps to arrive at a $CH_{2(ads)}$ C1 monomer after the adsorption of CO.[28] As shown in Table 1, they found that the least favourable was CO direct dissociation. The dissociation of CHO to CH is less favourable than *via* the more hydrogenated CH_2O intermediate, although it must be noted the activation energy to go from CO_{ads} and H_{ads} to CHO_{ads} is the same as the subsequent CHO_{ads} dissociation step, so although excluded by the authors it seems some CHO_{ads} dissociation may also occur. The large difference in overall barrier height between either Step 2 or 3 and Step 1 are, however, very striking. It must be remembered these results are for a surface that is known not to readily dissociate CO and so it is not clear how large the difference would be at more co-ordinatevely unsaturated sites. Nevertheless, as the authors point out, calculations for CO dissociation on corrugated and stepped sites are still significantly higher than for the steps *via* hydrogenated intermediates shown in the table.

Table 1. Summary of data from Ref. 28, showing activation energies of key steps in Figure 3.

	Mechanistic route	E_a calc. / $kJmol^{-1}$
Step (1) †	$CO_{ads} + * \rightarrow C_{ads} + O_{ads}$	272
Step (2)	$CHO_{ads} + * \rightarrow CH_{ads} + O_{ads}$	96.5
Step (3)	$CH_2O_{ads} + * \rightarrow CH_{2\,ads} + O_{ads}$	82.0
Route (2) †	$CO_{ads} + H_{ads} \rightarrow CH_{ads} + O_{ads}$	126
Route (3) †	$CO_{ads} + H_{ads} + ½ H_2(g) \rightarrow CH_{2\,ads} + O_{ads}$	126

† It should be noted that overall Routes 2 and 3 differ from Step 1 in starting point by one adsorbed hydrogen atom, so should not be directly compared.

They also use micro kinetic modelling to assess that only the route *via* Step 3, not Step 1 is relevant at both 0.05 mbar and 30 bar total pressure (although Step 2 is excluded, this would only further add to the preference for some form of indirect route). Another complication here is more recent STM work on cobalt nanoparticles supported on Cu(111) (the Cu surface here, which is unable to dissociate H_2, is used in place of a metal oxide support). This work showed H_2 can be readily dissociated at low co-ordination cobalt nanoparticle sites and spillover onto the low index cobalt facets (such as Co(0001)), but forms islands containing exclusively H_{ads} or CO_{ads}.[29] It was also shown that surface pressure from CO may force H_{ads} onto a Cu(111) support, which, like oxides, would not normally dissociate H_2 directly.[30] Calculating the actual surface coverage of H_{ads} becomes far from simple, since, if extra sources and sinks may exist for H_{ads} and the surface is not randomly ordered, it cannot then be viewed as a straightforward competition between adsorption of two molecules at a single cobalt metal site, as assumed in the above microkinetic models.

In support of the indirect mechanism, Iglesia and co-workers identified that the typical E_a reported for cobalt catalysts of 80 to 120 $kJmol^{-1}$ is not compatible with calculations for Co(0001) dissociating CO, but the argument that corrugated or stepped sites might behave more favourably is inconsistent with the particle size effect found experimentally (see Section 3), whereby Co sites on particles below ~ 6 nm are less intrinsically active (assuming only the size is changing).[31] Iglesia and co-workers also identified a further very important point concerning oxygen rejection selectivity. By careful consideration of the mechanisms in Figure 3, and the fact that CO is the overwhelmingly dominant surface species at catalytically relevant temperatures and pressures, it is apparent that whether water or CO_2 is formed from the oxygen shows which reaction sequence dominates. If CO is dissociated on the surface to produce O_{ads}, then the O_{ads} produced is overwhelmingly more likely to react with and be removed by another CO molecule than locating two H_{ads} species on the CO crowded surface required to produce H_2O. In contrast, in the indirect mechanism *via* Step 3 the oxygen is rejected to the surface as OH_{ads}, which requires only one H_{ads} for removal. It should be noted that the OH_{ads} cannot be reacting with CO to form CO_2 without there being a direct effect of hydrogen on primary CO_2 formation rates, which is not observed. For a Fe-Zn-Cu-K catalyst (where the iron and zinc largely form oxides), they demonstrated that the dominant oxygen rejection selectivity changes at pressures greater than ~ 2 bar and thus at typical operational pressures of ~ 20 bar suggests that the H-assisted *indirect* mechanism is dominant.[32] Much more recently, they have also identified the same indirect mechanism is favoured on Ru clusters and surfaces using DFT calculations.[33]

Further support for an *indirect* mechanism has also come from atmospheric pressure transient kinetic experiments on a cobalt magnesium catalyst by Schweicher *et al.* who showed a relationship between chain lengthening and gas phase CO pressure in the build-up of the reaction. They also identified that carbon surface coverage residual on the catalyst is not correlated with chain lengthening – in other words the reaction has no dependence on concentration of surface carbon as an intermediate, so only CH_x can be the 'C1 monomer.'

In contrast, this view is still controversial and microkinetic modelling by van Santen and Markvoort of atmospheric pressure Steady State Isotope Transient Kinetic Analysis (SSITKA) experiments for Ru and MnO promoted Co catalysts suggests the carbide mechanism to be in good agreement with the CO and CH_x residence times.

Since the complex mechanisms depend strongly on the nanostructure of the catalyst and the selectivity can be changed readily by any effect that may alter surface coverages (for example den Breejen *et al.* showed surface coverage of CH_x could be varied by both promotion with MnO and varying particle size) it is clear that understanding the atomic level structure of the catalysts is key in designing better (more efficient, selective) catalytic materials. The rest of this article focuses on what nanomaterials have currently been looked at to achieve this, and where they may play a role in the future.

3. Nanomaterials for understanding the importance of cobalt particle size and reducibility.

One focus area of considerable work is the issue of cobalt particle size. Typically in heterogeneous catalysis, metal particle size can be important for many reasons. At a simplistic level small particles should maximise the surface area and therefore provide potentially more sites for a given amount, and therefore cost, of metal. Small particles are also likely to have many more edge and corner sites which are co-ordinatevely less saturated and may exhibit different (beneficial or deleterious) activity. Geometrically it also increases the proximity of the metal surface sites to the adjactent oxide support – if the support material is non-innocent then this too will likely be a factor in the reactivity. Furthermore, specific / niche cases are known from heterogeneous catalysis more generally; two such examples are (1) the so called quantum size effect on very small gold particles (< 4 nm);[34] and (2) catalytic reactions involving large substrates, where the requirement for larger particles (> 10 nm) is attributed to the need to have large facets of low index surfaces available for the reaction to proceed.[35,36]

In the case of FT reactions, for some time it has been known that there was an invariant site time yield (reaction rate per site), but this was only the case over a certain range of metal dispersions; small particles < 5-6 nm were difficult to prepare and reduce to metal or were easily oxidised.[6] It was also noticed that measuring particle size was not straightforward, with TEM and magnetic measurements often conflicting with EXAFS (Extended X-ray Adsorption Fine Structure) spectroscopy and chemisorption characterization.[37] The same authors do however identify that particles that appear by TEM to be around 6 nm are the most active.[37] It is quite possible this discrepancy also resulted from the partially oxidised structure of smaller particles. By preparing a series of incipient wetness catalysts with carefully varied average cobalt crystallite size it has been seen that larger particles have a greater selectivity for the production of long chain hydrocarbons.[38] It should be noted that the same study (both on alpha and gamma alumina incipient wetness catalysts) saw no particle size effect in terms of site time yield.

In order to understand this issue more thoroughly nanomaterials are invaluable, since they afford routes to very tight size control of cobalt crystallites. This contrasts to all of the above studies with incipient wetness catalysts, which inevitably contained an appreciable range of different particle sizes and assume the 'average size' as representative. This is especially problematic with spectroscopic tools like EXAFS, which take a volume not a surface average. A number of routes have now been developed that allow for better control of particle size:

- carbon nanofibres (CNFs) with oxide defects to anchor / control particle growth during incipient wetness preparation;[39,40]
- reverse micelle synthesis and subsequent deposition of cobalt crystallites;[41,42]
- controlled decomposition of $Co_2(CO)_8$ organometallic cobalt in the presence of structure directing agents to form size controlled cobalt nanoparticles, again suitable for subsequent deposition on (or in) a support matrix;[43,44,45,46]
- controlled growth of cobalt clusters on 2-D planar surfaces using conventional surface science techniques;[11,47,48] and,
- polymer capping of nanoparticles, mainly used in solution phase FT synthesis reactions, where the polymers can be solubilised for reactant access.[49]

As shown in Table 2, the first four of these methods have yielded the clear result that small particles (below around 7 nm or less) are intrinsically less active (and where looked at also less selective towards higher molecular weight products). For CNF anchored nanoparticles at both 1 and 35 bar a significant decrease in site time yield was observed for samples with nanoparticles smaller than 6 nm.[39,40] CNF supports were selected to eliminate the possibility of oxide supports oxidising the cobalt. Using SSITKA the authors showed small nanoparticles had a greater fraction of sites occupied by irreversibly adsorbed CO. Reverse micelle synthesis was also used to prepare small cobalt crystallites in a zeolite (all crystallites ~ 4 nm). These were compared to a standard incipient wetness catalyst containing many different sized particles (average size 11 nm). The turnover frequency per surface site for CO conversion increased by over an order of magnitude between the 4 nm particles and the incipient wetness catalyst (average particle size 11 nm). The possibility of this being purely the influence of synthetic agents in the former was ruled out showing a ~ 6 nm sample, prepared in a similar way to the 4 nm sample, already exhibited a significantly higher TOF. Planar Co/SiO_2 samples have been obtained with very good particle size control using ultra high vacuum surface science approaches. When these were transferred to a high pressure reaction cell they show a similar trend with particle size[48] and exhibit catalytic behaviour in good agreement with conventional catalysts.[47] Notably, small particles were observed to be easily oxidised under reaction conditions.[48] Colloidally prepared nanoparticles depositied on silica, prepared *via* the organometallic wet chemical route, also yielded a similar overall trend in CO conversion.[44] It should be noted that the overall lower turnover frequencies in this case likely result from the presence of residual trioctylphosphine oxide from the particle synthesis, as was shown in a recent study by the author on CO_2 reduction using model cobalt catalysts, where a preferable, phosphorous free, synthesis is demonstrated.[46]

Table 2. Table showing TOF values for CO conversion during FT reactions for various cobalt crystallite size controlled catalyst samples.

Preparation Method	FT reaction Conditions	Sizes / nm	CO conversion TOFs / molecules.site^{-1}.s^{-1}
CNF anchored[39]	210 °C; 35 bar; $H_2/CO = 10$	2.7	1.1×10^{-3}
		6	1.1×10^{-2}
Reverse micelle[41]	220 °C; 20 bar; $H_2/CO = 2$	4.1	0.3×10^{-3}
		5.8	1.3×10^{-3}
Co/SiO_2 planar[48]	240 °C; 10 bar; $H_2/CO = 2$	< 3	6×10^{-3}
		> 3	5×10^{-2}
Cobalt/Oleic Acid[44]	240 °C; 10 bar; $H_2/CO = 3.3$†	3	0.6×10^{-3}
		10	1.9×10^{-3}
Incipient Wetness	210 °C; 20 bar; $H_2/CO = 2.1$	3.1–18 (av.)§	$4.7\pm1.6\times10^{-2}$

† Pressure quoted includes more than 50% argon reference gas. § Average sizes rather than samples containing discrete sized particles, no correlation with TOFs seen.

As surface oxidation could potentially occur in the reaction, it could be a key source of deactivation of the catalyst by reducing the number of metallic cobalt sites.[50] It appears a number of the above studies of cobalt indicate reducibility to be an issue with smaller particles. This could occur in two ways. Firstly, it could be that the cobalt is never reduced fully during the activation steps; these are not conducted at higher temperatures to avoid agglomeration.[6] For pure cobalt nanoparticles of 4 nm a fundamental study following oxidation of the cobalt nanoparticles using *in situ* Near Edge X-ray Adsorption Fine Structure (NEXAFS) spectroscopy has shown that 1 bar of H_2 at 250 °C is insufficient to reduce the cobalt to the fully metallic state.[51] Secondly, the re-oxidation of cobalt has been proposed to occur under reaction conditions. Goodman and coworkers looked at planar Co/SiO_2 and identified by post-reaction XPS that small particles are significantly oxidised under reaction conditions, but not by CO alone.[48,52] They therefore attribute the re-oxidation of the very small (< 3 nm) cobalt particles to water produced during the reaction. NEXAFS spectroscopy has been used to look at 4-5 nm cobalt crystallites on silica (prepared by spin coating) in a 1:1 mix of H_2O and H_2 at a total pressure of 0.4 mbar and over all relevant temperatures; no oxidation of cobalt occurred (although it is not clear if a higher partial pressure of water could still be the cause of oxidation).[53] However, since neither water or CO alone appear to oxidise cobalt it could of course be the case that instead of oxygen residual on the surface from direct CO dissociation as proposed previously,[25] the oxidation occurs from hydrogen activated CO dissociation (the indirect mechanism). This would therefore not be seen in any of these experiments without both CO and H_2 present, but still result in an oxidised surface under reaction conditions. A further study of a mixture of a reduced Co metal and an oxidised CoO conventional catalyst that becomes more reduced under 20 bar / 230 °C reaction conditions over time appears to conflict with the above results; however, as this catalyst is Pt promoted it may behave differently with respect to reduction of the cobalt (see below).[54]

Overall the ability to prepare nanoparticles of well-defined sizes (*e.g.* samples with a particle size distribution of only ± 0.5 nm[46]) by a selection of routes has confirmed a particle size effect exists. This is likely to be important in the design of practical catalysts for FT synthesis. Further work is needed to clarify if this is purely related to reduction and oxidation of cobalt, or possibly the result of irreversibly bound CO. Size controlled nanomaterials will hopefully aid the further exploration of such questions.

4. Role of support and support porosity using nano-controlled support materials.

The role of the support in FT reactions has generally been thought to be unimportant; the site time yield or per site reaction rate is found to be invariant across a large range of different supports.[6] Typically alumina is used as the support material for cobalt FT synthesis catalysts, just as for many other heterogeneous catalysts. It should, however, be noted that early FT catalysts were prepared on mixtures of thoria and Kieselguhr (a type of silica material formed from aquatic organisms in sedimentary rock). Even on very different alpha and gamma alumina supports the choice of support for a given particle size is unimportant.[38] However, although the role of the support seems unimportant to the activity of the catalyst, it can nevertheless be important in the material's preparation. At this stage it can impact considerably on achieving the desired metal particle size. For impregnated catalysts a competition exists between binding cobalt precursors weakly enough to be easily reduced yet strongly enough so cobalt diffusion and subsequent agglomeration does not occur. Strategies for achieving this balance have included using citrate ions to change the precursor-support interactions so that reduction occurs at low temperature and diffusion is slow,[55] or using TiO_2 to bind the metals more tightly and offsetting the lower extent of reduction with the fact that overall a higher surface area exists because agglomeration is prevented.[56] In the latter case the use of TiO_2 was also found to improve long chain hydrocarbon selectivity. Using TiO_2 is complicated by the strong metal-support interaction (SMSI) type effects seen after high temperature reduction, which forms TiO_x overlayers on the metal particles, changing the adsorption of reactants on the surface. Whether this is an important effect is a matter of debate as water produced under reaction conditions may be able to remove the overlayers formed.[6]

Using nanomaterials brings a considerable advantage in trying to understand the role of supports in FT chemistry in that it allows for discrimination in the preparation steps from any metal-support interaction. This can now be achieved because the metal particles can be manufactured separately and only subsequently placed into the support material. Furthermore, through molecular templating of the support materials well defined supports can be produced and one particularly important area is the design of uniformly ordered porous materials. Pore size constraints are known to be important from attempts to put cobalt into zeolites, in which the chain length was found to be limited to around C_{11}.[57] Model cobalt core / silica shell nanoparticles also caused a reduction in the product chain length as the thickness of the silica shell increased.[58] In addition to product diffusion, confinement may also prevent growth and sintering of the cobalt particles during reactions.

Ordered mesoporous silicas containing pores of varying pore size have been used to systematically study the impact of pore size related effects. Pore sizes studied include small pores (MCM-41, pore diameter ~ 3 nm; SBA-15, pore diameter ~ 9 nm) though to large pore commercial silicas (average pore diameter 33 nm).[59,60,61] The main trend appeared to be that small pores prevented the growth of large particles (including during reaction) and resulted in small, hard to reduce cobalt particles. Although this appeared to favour longer chain length, caution must be taken in attributing the effects to either particle size effects or diffusion effects and is a matter still under investigation. Large templates such as the polysaccharide chitosan have enabled bimodal pore size distributions to be prepared in the same hierachical materials[62] – their behaviour is attributed to purely diffusion effects, but again sintering resistance could also be important.

Another class of mesoporous materials that has been an area of significant research (at least in the laboratory) is ordered carbon materials, such as nanotubes and ordered mesoporous carbons (*e.g.* CMK-3, an inverse SBA-15 structure template by using SBA-15, then removing the silica with aqueous HF). With these materials the importance of pores in controlling growth and sintering resistance has also been demonstrated by comparison to both commercially available activated carbons,[63,64] and the mesoporous silica systems described above.[65] However, it has been proposed that the electric field in the curved carbon support may facilitate electron removal in the case of smaller particles and more tightly curved nanotubes, making reduction of the cobalt to the active metallic form easier.[63,64] This is still a matter of some debate as Tao and co-workers recently identified that varying the reduction temperature and looking at particles inside and outside the pores (opposite curvatures) allowed them to achieve the same extent of cobalt reduction at 400 °C on both concave (internal) and convex (external) surfaces.[66] Another potential issue of using carbon materials is that diffusion leading to cobalt sintering may be harder to prevent. For iron based catalysts, oxygen containing defects on the carbon nanotubes have been identified as 'docking sites' for nanoparticles, allowing them to be pinned and preventing diffusion and subsequent sintering.[67] The same idea has been put forward for carbon nanofibre supports in which surface oxygen groups are thought to cause better cobalt dispersion on the support.[68]

Nanomaterials synthesis has also been used to prepare systems that specifically target activity or selectivity such as cobalt particles on 'alumina nanoparticles / carbon nanotubes' or 'TiO_2 decorated SiC' composite supports.[69,70] Although improved reducibility and catalyst stability have been claimed for these materials, their complexity makes it challenging to identify confidently the molecular level roles of each of the different components.

5. Precious metal promotion effects studied using nanomaterials.

A final and crucial area where nanomaterials are playing an important role in understanding FT chemistry is in elucidating the role of precious metal promoters. These are extensively used, with most catalysts containing at least one precious metal promoter.[71,72,73,74] The role of these promoters has been attributed to a variety of possible effects – as summarised by Iglesia who points out these can be classified as structural and chemical promoters that increase the number of active sites and the activity per site respectively.[6] Owing to the cost and limited availability of these metals, understanding the role of such materials and, therefore, how they could be reduced or replaced is of paramount importance for the widespread use of Fischer-Tropsch. It was argued for the Ru-promoted catalysts studied that at least some fraction of the effect is 'chemical' as a Ru/Co ratio of 0.7 atom % was sufficient to promote the reaction.[6]

The general effect has been postulated to be due to many factors, including: (1) intimate electronic contact changing the local band structure of the metal; (2) ensemble type geometric effects; (3) reducing deactivation by carbonaceous deposits; and, (4) enabling more surface sites to be reduced by hydrogen spill-over during the initial activation. Attempts to use aberration corrected STEM (Scanning Transmission Electron Microscopy) for a series of cobalt alumina catalysts promoted by Ir, Pt, Ru and Re show the complexity of the problem. In each case a promotional effect on the reaction was seen, however Pt, Re and Ir appear as isolated atoms in the Co particles' surfaces while Ru appears in clusters. Furthermore, there is evidence for hydrogen spill-over in the promoted catalysts, since even cobalt particles containing no precious metal atoms appear more reduced than for cobalt particles in samples without precious metal additives being present at all.[75] Systematic studies of Ag, Au and Rh promotion of Co/SiO_2 catalysts have shown that only very small quantities of the promoter are needed (Rh/Co ratio = 0.7 wt. %). It was argued by the original authors that clusters of surface Rh atoms were able to increase the hydrogen coverage and thus the availability of C1 monomers on the surface.[76] Similarly, in the case of gold promotion, it has previously been identified that an optimum Au/Co ratio exists as the favourable promotional effects are offset by the unfavourable water gas shift activity of gold (Au/Co ratio = 10 wt. % was optimal).[77] EXAFS studies on incipient wetness and sol gel type Pt promoted catalysts appear to indicate the existence of intimate contact betwen Pt and Co as there is no evidence for Pt-Pt bonding.[78,79] Re appears not to promote cobalt reduction until the Re itself has been reduced.[80] In all three cases the role of Pt or Re in initially reducing the cobalt is implicated in the mechanism of promotion. The challenge here, however, is in trying to look at EXAFS data averaging over a sample where only trace amounts of platinum are present and a range of particle sizes and levels of Co-Pt mixing could be present in different regions of the sample.

One approach to investigate this problem is by using highly uniform nanomaterials. Pt-Co bimetallic nanoparticles of uniform size and composition have been prepared and their reduction and oxidation investigated. This has been done using in situ techniques such as ambient pressure XPS / TEM and atmospheric pressure EXAFS / NEXAFS. In the first instance, this promisingly reveals correlations between improved Co reducibility and the presence of the platinum.
[51,81] However, subsequent investigation using ambient pressure XPS and environmental TEM showed that Pt-Co nanoparticles in reducing atmospheres (such as during the Fischer-Tropsch reaction) segregate Pt to the surface. The Pt then covers the particle surface as shown in Figure 4.[82] These Pt encapsulated particles were found to be completely inactive for CO_2 hydrogenation.[82] It was reported that preparing nanoparticles of consistently low Pt concentration is synthetically very difficult owing to their segregation into particles with and without Pt. This could point to the role of Pt promoters being less straightforward than anticipated as the Pt and Co are also likely to have segregated in the same way in the incipient wetness preparations. The role of the Pt could instead result from inter-particle hydrogen spill-over between Pt rich particles and pure Co particles. This idea of inter-particle H_{ads} diffusion is in agreement with the mechanism identified in the aberration corrected STEM study mentioned previously.[75]

Other possible alloying metals (non-precious) have been looked at using the same colloidal nanoparticle approach, in particular CoCu alloys. These have also been identified to restructure dramatically under reducing and oxidising conditions through the use of ambient pressure XPS and *in situ* NEXAFS.[83,84] The combination of Co and Cu is being investigated in a number of laboratories and, if better understood, can be seen as a likely choice for attempting to harness the alcohol synthesis characteristics of Cu (used in methanol synthesis) and the chain growth FT behaviour of cobalt to produce higher alcohols. This has been seen with both co-precipitated catalysts[85] and those prepared *via* metal oxalates.[86]

6. Conclusions and Future Perspectives

Overall, nano-materials based catalysts – whether from nanoparticles, from template oxides, or from the combination of the two – have already afforded a number of insights into the fundamental chemistry that underlies the Fischer-Tropsch process. Specifically, they have been used to show the importance of the cobalt particle size owing to the difficulty of reducing very small nanoparticles; the importance of oxide pore size in controlling growth and diffusion and the likely role of hydrogen spill-over in the precious metal promotion that is widely used in commercial catalysts. The ability to tune nanoparticles and compare series of materials prepared in a like manner provides a valuable way to inform our thinking about how catalytic systems work at a molecular and atomic level. A number of challenges however remain. There is still not a universally agreed upon mechanism as to what route the catalysis occurs *via* and whether this is the same on all catalysts. More synthetic approaches are needed to prepare bimetallic materials for exploring promotion and co-operativity between different metals, such as CuCo mentioned above. There also needs to be clarity as to how the residual reagents from the nanomaterials are removed so they cannot be accused of interfering with catalysis or altering the result of such model studies. Finally, as we look to utilise a higher proportion of biofeedstocks, much more knowledge is needed of poisoning mechanisms and how sulfur, alkali and nitrogen containing species deleterious effects[87] may be minimised through the rational design of poison tolerant catalysts. Many challenges in FT chemistry are still to be solved in its application to the global energy crisis. The role nanomaterials can play in achieving this but improving our molecular and atomic level understanding, and enabling the subsequent rational design of improved catalysts, appears to be becoming of indisputable importance.

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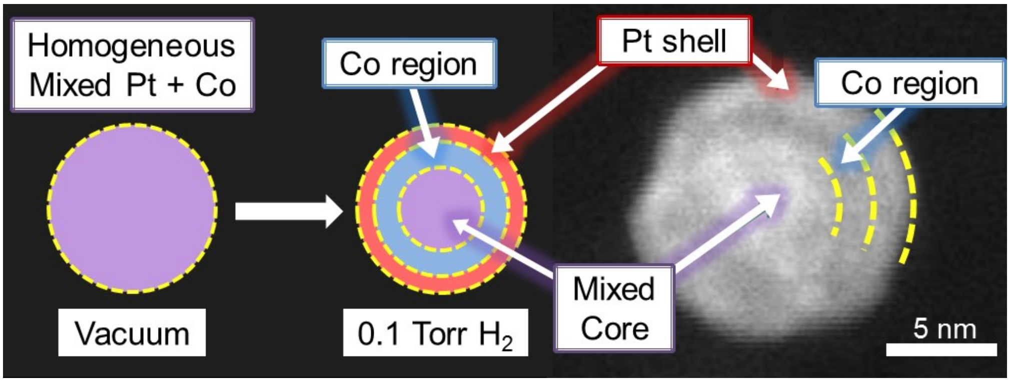

Figure 4. Environmental Transmission Electron Micrograph (Reproduced with permission from reference 82) of a PtCo nanoparticle (right), obtained under 0.1 Torr H_2 gas using Z-contrast imaging. This technique results in brighter regions for Pt than Co (per atom) and so the bright halo around the particle shows the segregation of platinum and cobalt in the near surface region, as shown in the adjacent schematic (left). As reported in reference 82 the structure in the schematic was confirmed by depth profiling the nanoparticles under the same conditions with Ambient Pressure XP Spectroscopy.

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Author Biography

Simon K. Beaumont

Simon Beaumont received both undergraduate (B.A. / MSci) and PhD degrees in chemistry from Cambridge University. He studied for his PhD under the direction of Prof. R. M. Lambert, focussing on application of nanoparticles to heterogeneous catalysis. He then moved to the University of California, Berkeley, as a Postdoctoral Research Scholar with Prof. G. A. Somorjai. There, he investigated cobalt and bimetallic nanoparticles for CO/CO_2 hydrogenation, and their study using synchrotron radiation techniques. He is now (since 2010) a Lecturer and Leverhulme Trust and Addison Wheeler Fellow at Durham University, UK, where his work continues to include Fischer-Tropsch chemistry.

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Table of Contents Graphic and Abstract:

This perspective offers an overview of using nanomaterials for improving our understanding of the underlying mechanism of cobalt catalysed Fischer-Tropsch chemistry. This is considered in terms of enabling the rational development of improved (more selective, efficient, longer lived) catalysts.