Dark material with a bright future: Carbon as support in future heterogeneous catalysis – A short personal perspective

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ABSTRACT

The increasing concern for the environment has spurred research into the use of new feedstocks such as biomass and CO_2 for the sustainable production of chemicals and materials. Here I will show, based on selected examples of own work on electrocatalytic and thermocatalytic glucose and starch oxidation, CO_2 capture and lipid deoxygenation that carbon supports are eminently suitable for studying particle and support effects when converting these new feedstocks. In addition the replacement of noble metals by Mo-carbide and W-carbide, i.e. more readily available non-noble metal based catalysts, will be demonstrated for carbon based supported carbides. These examples highlight the relevance and potential of carbon supports in future catalysis.

1. Introduction

Heterogeneous catalysts are the workhorse of the chemical industry. In more than 80% of all industrial processes one or more catalysts are used [1] of which 80% [2] are heterogeneous catalysts.

In general, a heterogeneous catalyst consists of a support, one or more active phases and optionally promotors. The interplay of all these components determines the performance of the catalysts. To arrive at a rational design of catalysts, understanding of the functioning of the catalyst and the role of the different components in that functioning is essential.

For the support many options are available like amorphous oxides, nanoporous crystalline oxides (zeolites), mesoporous oxides and others. Here the focus will be on carbon supports since they are relevant for fundamental understanding and applications of catalysts as has been reviewed earlier [3–6]. Carbon has several advantages which makes it a suitable material as catalyst support. The most noticeable ones are its inetrness especially in aqueous conditions and its tunablity via surface chemistry, issues which will be used here as well. In addition, supported metals can be easily reclaimed by burning the carbon. This also is one of theownsidees of carbon, it is not very resistant to high temperatures and oxidizing conditions though this does depend on the type of carbon (carbon nanofibers can be heated in air to about 350 °C without full combustion). Carbon exists in many forms like activated carbon, graphite, graphene, and nanostructured carbons like nanotubes, nanofibers, nanohorns, nano-unions and nanodiamant [5].

For catalytic applications activated carbon is the workhorse since it is cheap, readily available and has a high surface area. Nevertheless, the microporosity of that material together with the presence of (difficult to control) heteroatoms (as a result of the use of natural sources to make the activated carbon) makes the use of that carbon for fundamental understanding of the other components of a catalyst more challenging. Graphite on the other hand is a pure carbon yet natural graphite has a low surface area which hampers its use in catalysts. The nanostructured carbons like carbon nanofibers and nanotubes and the now available high surface area graphite overcome these challenges i.e. they are pure and have a high surface area [3,4]. Thus, these materials are eminently suitable for fundamental catalytic studies while the activated carbon is already applied in the chemical industry which highlights both the fundamental and applied relevance of carbon.

In this perspective I will highlight some of the recent advances achieved in catalysis by the use of carbon materials as a support. I will use results of my group as a guide for that. In retrospect the topics dealt with in the 2010 review [4] i.e., particle size effects and support effects, remain relevant also with change in the catalysis landscape (see next chapter). In addition the replacement of noble-metals with more readily available elements did become more relevant due to the scarcity of the noble-metals [7]. Some example of using non-noble replacements will be discussed. Here I will discuss the use of Ni on carbon nanofibers for aqueous phase processing and the replacement of supported Pd catalysts by carbon nanofiber supported molybdenumcarbide and tungstencarbide.

2. Change in the catalysis landscape

Though the use of fossil oil as feedstock is already known for about 2000 years it is since the last 150 years that the use of fossil resources, gas, oil and coal, became indispensable for daily life. Yet the increasing awareness of the negative environmental impacts of using fossil resources has spurred vivid research into alternative feedstocks. These alternative feedstocks must be sustainable and should, preferably, be convertible into molecules with similar or better properties as those currently used.

For making chemicals and materials not many alternative feedstocks are available since a prime requirement is the presence of carbon in the feedstock. Therefore, possible options are biomass, CO_2 and waste streams (e.g., plastic recycling). Please note that for fuels also carbon is needed but that these fuels are often used for energy purposes and for that in many cases, though not in all as in heavy transport and planes, alternatives based on electricity (wind, solar, water) are more attractive. In any case big changes are needed in our way of thinking on feedstocks and catalysis [8].

A major challenge for converting these new feedstocks, especially biomass and CO_2, is the fact that they contain carbon in a higher oxidation state, i.e., more oxygen is present, compared to the carbon in the fossil feedstock (Table 1). This means that to make the molecules we are currently used to, i.e. the so called drop-in molecules, the feedstocks need effectively to be reduced. While fossil feedstocks, in general, need to be oxidized. Obviously, the chemistry a catalyst must perform has to change as well when making drop-in molecules. Alternatively new molecules can be made out of the new feedstocks. An example of that is the replacement of the monomer terephthalate by the furanoate FDCA (2,5 furan dicarboxylic acid) in polymers. From the terephthalate FDCA can be made from renewable sugars and this requires oxidation chemistry [11]. Thus, also when using biobased feedstocks oxidation reactions remain relevant next to reductions/deoxygenation. The quest for more sustainable production does not only influence the choice of feedstocks and products, the latter because reuse/recycling needs to be incorporated in the design of the products to make, but also holds for the catalyst. Often catalysts, and I will limit myself to heterogeneous catalysts, are based on noble metals for good reasons. Noble metals are active and more importantly stable under a wide range of reaction conditions. Especially with the new feedstocks (biomass) and energy inputs (electricity) stability in water is essential. However noble metals are scarce and as a result expensive therefore non-noble alternatives need to be sought for.

In addition to stability of the active phase also the stability of the support is essential. Fig. 1 shows that this can indeed be an issue during aqueous phase processing of biomass.

In that study we showed a.o., that the BET surface area of a number of typical supports decreased significantly under hydrothermal conditions relevant for aqueous phase processing of polyols towards H_2 and carboxylic acids [13–15].

Carbon and especially carbon nanofibers are stable under most biomass relevant conditions. That is why we often use that support as a model support. In addition, carbon and carbon nanofibers are conductive which makes it eminently suitable for electrochemical applications. Nevertheless, some care needs to be taken under (strongly) oxidizing
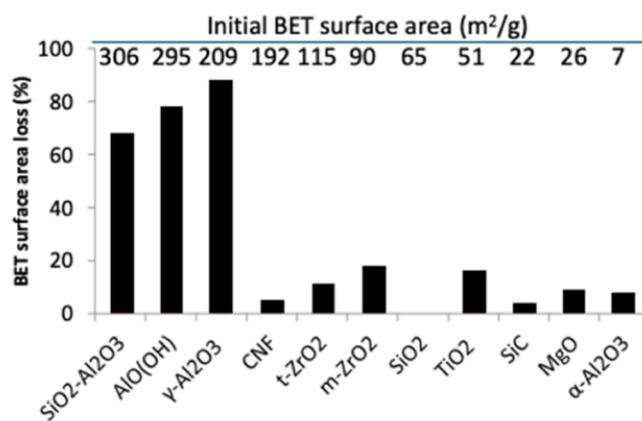
Fig. 1. Surface area loss of different supports under hydrothermal conditions (autoclave, 200 °C, 20 h), (based on van Haasterecht [12]).

conditions since under these conditions the catalyst might not be stable. Yet for biomass conversions even oxidations, and electrochemical biomass conversions including oxidation, carbon is a suitable support as will be shown below.

3. Types of carbon in catalysis

Different allotropes of carbon exist. From a catalyst support point of view I categorized them in three important classes i.e., the activated carbons, the graphites and the nanostructured carbons (Table 2). Table 2 gives a generalized summary of the pros and cons of these different carbons where for the nanostructured carbons I focus on carbon nanofibers. The reason for that is that carbon nanofibers (CNF) can be made in relatively large quantities and as materials with a high bulk density and bulk crushing strength [16]. That latter two are clear advantages for catalysis. Nevertheless other nanostructured carbons also have their merits of which the lower density is an advantage of carbon nanotubes for visualizing supported particles for example by TEM (which is more difficult with the dense carbon nanofibers). [17].

Though CNF are suitable catalyst supports as result of their properties their industrial application is still hampered by their high price which is the result of their laborious preparation. The preparation, in general, involves the use of a growth catalyst (e.g. Ni/SiO2, Co/Al2O3) which is exposed to a carbon containing gas at high temperature [3]. After growth of the CNF the growth catalyst is removed by acid and base treatments to obtain the carbon material. Further oxidation treatments can be applied to introduce reactive groups on the surface which can ease the deposition of active phases [18,19] or act as active phase itself [20].

Although for a direct industrial application CNF are not used yet they are eminently suitable for catalysis studies. The lessons learned from using these carbon materials can then be used as input of further catalytic studies on other supports as for example shown in the past for Fischer Tropsch synthesis. Particle size effects were investigated using Co/CNF catalysts which gave insight in the optimal particle size for Co

Table 1

Typical comparison of biomass and oil, numbers give an indication, exact numbers depend on the specific feedstock.

Element	Biomass (wt%) [9]	Oil (wt%) [10]
C	50	85
H	6	12
N	0.4	0–1
O	35	0–2
S	0.2	0–6

Table 2

Comparison of relevant carbons as support material.

	Activated carbon	Graphite	Carbon nanofibers
Preparation	carbonization of natural sources	natural material or graphitization[a]	chemical vapor deposition
Surface area	500 m²/g	1–10 m²/g	100–200 m²/g
Porosity	microporous	non porous	mesoporous (between fibers)
Heteroatoms	present	absent	absent
Reactivity	high	low	low

[a] Synthetic high surface area graphites (150 m²/g) are also available

[21]. Later this knowledge was used to study optimal particle sizes on a support which can react with Co i.e., SiO_2 [22].

4. Use of carbon as catalyst support in emerging fields - outline

Metal particle size effects and support effects are important topics in heterogeneous catalysis to steer the performance of a catalyst. This has been studied often in the past for a wealth of reactions like Fischer Tropsch synthesis [21,22] and other hydrogen assisted reactions [23].

In this perspective I will focus on particle and support effect studies with activated carbon and carbon nanofiber supported catalysts for the conversion of biobased feedstocks (glucose, starch) both thermochemically and electrochemically. I will also demonstrate the insights obtained using carbon supported K_2CO_3 for CO_2 capture. Finally, I will highlight the potential of carbon nanofiber supported Mo-carbides and W-carbides for deoxygenation lipid based feedstocks.

5. Glucose and starch oxidation over Pt/activated carbon and Pt/CNF

5.1. Chemical oxidation of glucose over Pt/activated carbon

Oxidized starch is a potential (and already commercial) sustainable replacement of polyacrylates which are fossil based. These products are used as super absorbers e.g., in diapers and in wastewater treatment.

Oxidized starch also finds applications as thickener in food. To arrive at the oxidized starch currently homogeneous oxidation using hypochlorite is used [24]. In addition, the use of homogeneous catalysts and peroxides are also explored [25]. The use of air (or maybe oxygen) and a heterogeneous catalyst potentially solves some issues of the current processes with respect to catalyst recovery and formation of byproducts (e.g., salts). However, large molecules like starch might adsorb too strongly on the catalyst to be effectively converted. Please note that starch needs to be solubilized by pressure cooking as is currently routinely applied in industry before it can be converted. Though this solubilization is commercial practice on large scale it adds an additional step and thus additional costs to the process.

In addition to starch oxidation also glucose oxidation, a building block of starch, is interesting since it produces, after double oxidation, dicarboxylic acids which are interesting building blocks for polymers. For both reactions the property-performance relationships have not been studied before which are needed to arrive at better catalysts.

We have investigated the role of Pt particle size and support polarity, the latter modified by introducing oxygen groups on the carbon surface by oxidation in nitric acid using Pt/activated carbon.

Fig. 2 shows representative TEM micrographs of the four prepared catalysts. Clearly samples with larger and smaller average particle sizes were prepared [26]. In addition also the support polarity was varied between the samples as was established by TPD and XPS [26]. When the performance of these 4 catalysts is compared (Fig. 3) it is clear that the
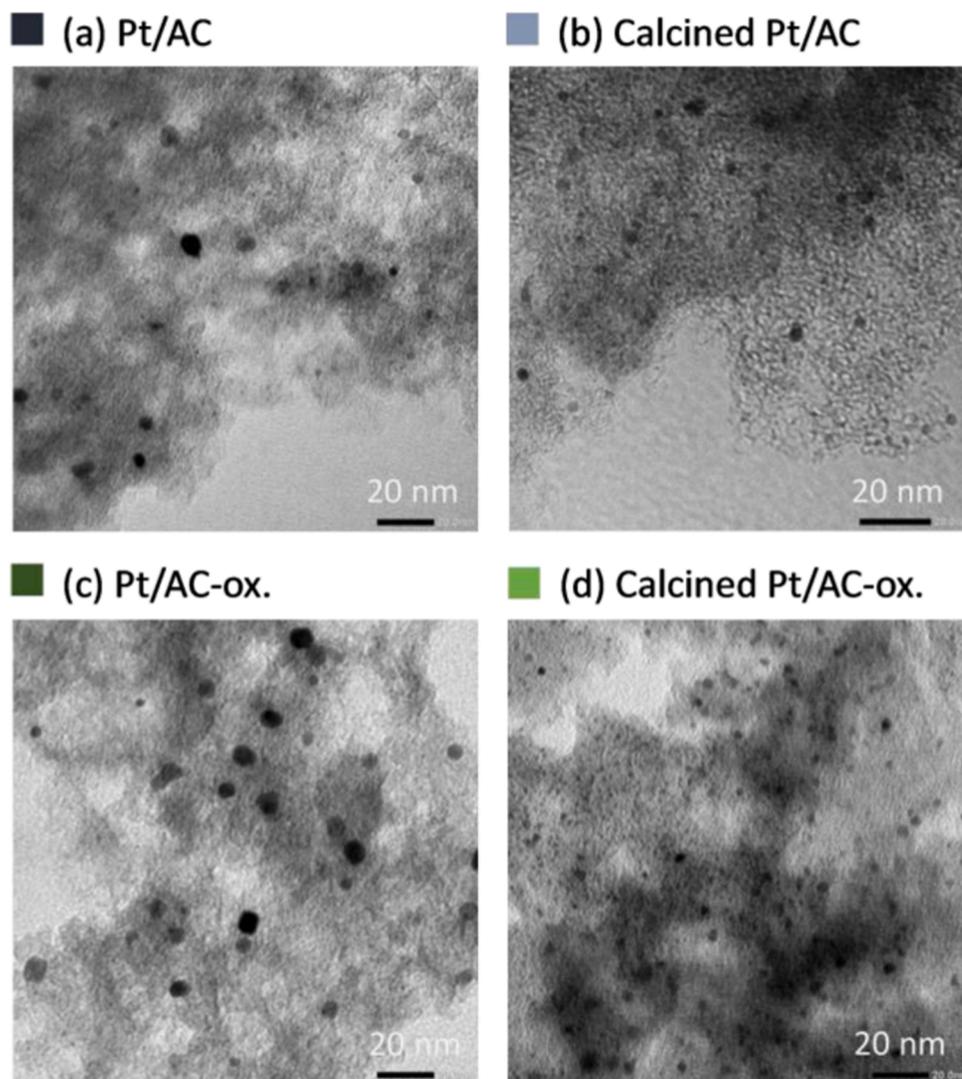

Fig. 2. Representative TEM images of (a) Pt/ AC Dav= 3.4 nm (non treated activated carbon (AC), Pt-precursor directly reduced after impregnation), (b) calcined Pt/AC Dav= 2.5 nm (non treated activated carbon (AC), Pt-precursor first calcined than reduced after impregnation), (c) Pt/AC-ox Dav= 3.6 nm (HNO3 treated activated carbon (AC-ox), Pt-precursor directly reduced after impregnation) (d) calcined Pt/AC-ox Dav= 1.8 nm (HNO3 treated activated carbon (AC-ox), Pt-precursor first calcined than reduced after impregnation), reproduced with permission from [26].
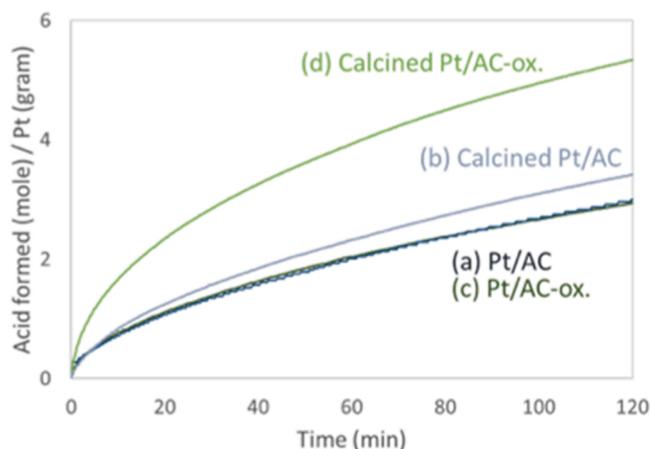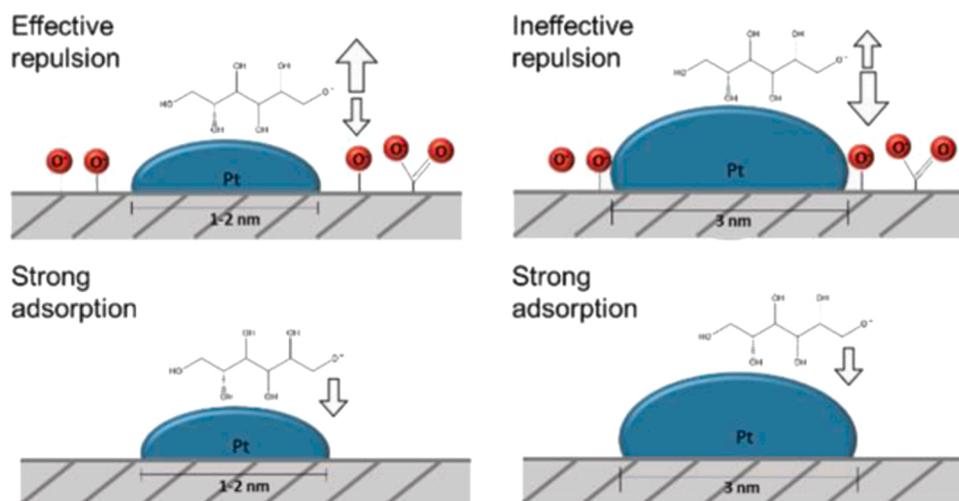
Fig. 3. Kinetic curves for glucose oxidation as measured by titration of the formed gluconic acid over AC supported Pt catalysts. Reactions were performed at 50 °C, pH 9, 0.05 M substrate concentration, stirring speed of 2000 rpm and an oxygen flow rate of 300 mL/min.
[reproduced with permission from [26].

Fig. 5. Principle of paired electrolysis reproduced with permission from [27].

sample with a high support polarity (higher number of oxygen groups) and small Pt particle size (calcined Pt/AC-ox) shows the highest activity (TOF). Since XPS and XANES did not indicate differences in the electronic structure of Pt we concluded that the support assists in adsorbing the reactant which is most pronounced on small particles with a polar support (Fig. 4). Thus a polar support with a high adsorption capacity for the reactant and small Pt particles which result in a high number of active sites results in the optimal catalyst.
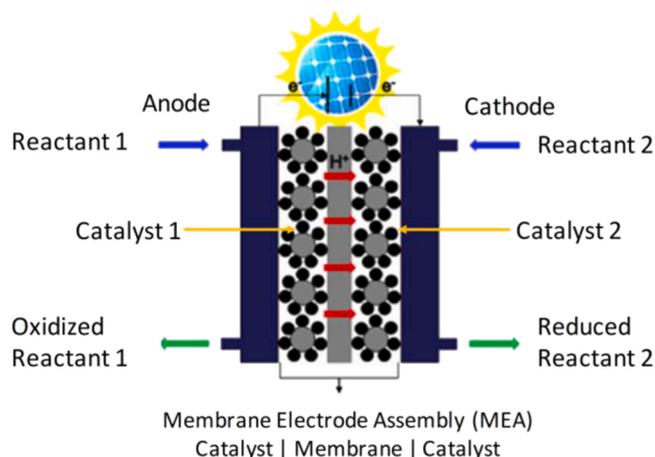
5.2. Electrochemical oxidation of glucose and starch over Pt/CNF

Electricity is regarded as the most promising sustainable energy carrier for the future. When implemented on a large (industrial) scale catalytic conversion processes have to be rethought. A possible approach is to make two usefull products in an electrochemical reaction i.e. the so called paired electrolysis (Fig. 5 [27]).

Electrocatalysis attracted significant attention in the last years. Especially the conversion of CO_2 to chemicals and fuels has attracted wide attention. However, making more complex molecules from CO_2 is still a big challenge. In that respect the use of molecules delivered by nature, which are also based on CO_2, might be a viable option.

When looking at the literature for the electocatalytic conversion of larger molecules it seems that most electrodes used are based on poly-crystalline (bulk) metals. Though that gives valuable insights the efficiency of metal use is not high. By the use of carbon supported metal nanoparticles the use of metal is more efficient, i.e. higher activity per gram of metal. Moreover steering catalytic performance via particle size and support effect becomes possible. The downside of a porous support is the potential mass transport limitation. Mesoporous carbon like CNF already decreases the risk of mass transport limitation due to its larger pore size.

Fig. 6 shows the linear sweep voltammograms of 4 Pt/CNF which differ in their content of surface oxygen while the Pt particle size slightly differs (1.3–2.0 nm). Operando XANES confirmed that in all catalysts the Pt was in the same state. Thus the difference in activity (with gluconic acid as the major product) was attributed to an enhanced adsorption of the reactant on the support, most likely those at the support-particle perimeter. This claim was further supported by the fact that the calculated number of sites on the Pt-support perimeter in different samples scaled well with the activity. Please note that the oxidation is a complex process where at 0.4 V gluconolactone is formed while at higher potentials gluconolactone is further oxidized to different products.

Preliminary results in which we tried to electrochemically oxidize solubilized starch were also positive. Fig. 7 shows a linear sweep voltammogram of the electrochemical starch oxidation. Clearly around
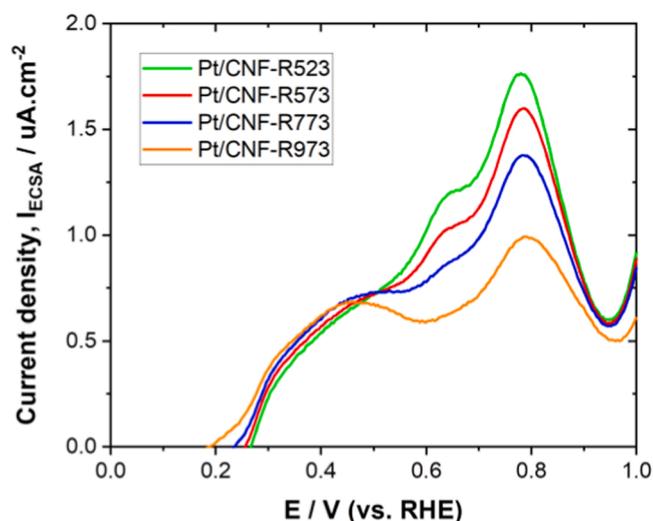

Fig. 4. Adsorption of glucose on small vs. large Pt particles and oxidized vs non-oxidized AC surfaces.
[reproduced with permission from [26].

Fig. 6. LSV of glucose oxidation, surface polarity increased going from R973 (K)-R523 (K), the activity increased in the same order (Single cell, Room temperature, pH=1 0.1 M H_2SO_4, 0.1 M glucose)[vd Ham, Bitter to be published].
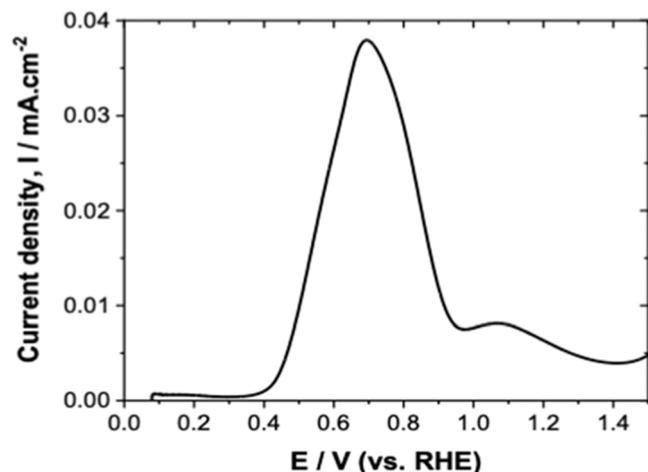

Fig. 7. Linear sweep voltammetry of starch oxidation using a polycrystalline Pt electrode (Single cell, Room temperature, 0.1 M phosphate buffer, pH=11.5, 0.1 M starch (monomers)) [vd Ham, Bitter to be published].

0.7 V an oxidative current has been observed. The selectivity of that reaction i.e. the extend of oxidation of the starch and the position of the carboxylic groups in the starch molecule are currently under investigation.

5.3. CO_2 capture using K_2CO_3/carbon

With the rising concentrations of CO_2 in the atmosphere which are related to temperature increase the concern for these CO_2 concentrations is also increasing. CO_2 capture is one of the pathways to mitigate the CO_2 level increase. The capture of CO_2 can be performed in many different ways of which flue gas capture i.e., at the exhaust of a point emitter and direct air capture i.e. capture of CO_2 from ambient air are two important strategies. The principle of CO_2 capture relies on the fact that CO_2 is an acid and therefore adsorbs on a base. However, the base should not be too strong since for an efficient process the CO_2 needs to be desorbed and further used (CCU) or permanently stored (CCS). The stronger the base the more difficult it is to desorb the CO_2. In the past we have shown that K_2CO_3/CNF were promising materials for flue gas

capture due to the relative low temperature of CO_2 desorption from these materials [28].

Recently direct air capture became more in focus. We investigated the role of K_2CO_3 particle size and the role of support polarity on the performance of K_2CO_3 on carbon black and activated carbon respectively. Estimation of the K_2CO_3 particle size on Ketjen black turned out to be (and still is) a great challenge. The contrast in TEM is too low to visualize the particles and their amorphous nature hampers the use of XRD. However, by using TEM after burn-off of the carbon combined with melting point depression some trends could be seen in the particle size with increasing K_2CO_3 loading (Table 3 [29]). By increasing the K_2CO_3 loading from 10 to 50 wt% the K_2CO_3 particle size increased from 120 to 1000 nm. This in turn had an influence on the capture rate and penetration depth of CO_2 into the K_2CO_3 particle (Table 3). All samples adsorbed about 0.4–0.5 mol CO_2/mol K_2CO_3 which is half of the expected capacity. This is however independent of the particle size. That is surprising since this means that the penetration depth of CO_2 for the small particle is less compared to that of the larger particles. The underlying mechanism for this is not clear yet.

The influence of support polarity was also investigated for K_2CO_3 on carbon [30]. In this case two microporous activated carbons CA1 (Norit) and SX ultra (Cabot) were used. The textural properties of these two carbons are very similar but the CA1 has a much higher density of acidic surface groups (PZC=2) while SX ultra is neutral (PZC=7). After depositing 10 wt% K_2CO_3 on both carbons the CO_2 uptake was measured via breakthrough experiments (Fig. 8).

Clearly the sorbent with the more apolar support (SX ultra) has a lower sorption capacity (i.e. earlier breakthrough) compared to the more polar support. We attributed that to preferential adsorption of water on the too polar surface of the CA1. As a result, the CO_2 capture capacity is decreased. It is important to note however that water is essential for the adsorption reaction (overall reaction K_2CO_3 $+H_2O+CO_2 \rightarrow 2KHCO_3$). Therefore, an optimum polarity is expected which is currently under investigation.

6. Replacement of noble metals

In general, noble metals are still preferred as catalysts due to the excellent stability and activity. However, their scarcity and limited availability in sometimes politically less stable parts of the world asks for a diversification of active catalysts. Non-noble metals like Ni and Fe are obvious choices though their stability in for example the aqueous conditions often applied in biomass based conversions is questionable. However, we showed, for Ni/CNF for aqueous phase processing, that this depends on the applied reaction conditions. The most likely mechanism for Ni particle growth is Ostwald ripening which involves dissolution of smaller Ni particles and precipitation of the dissolved Ni-species on larger particles. Since the dissolution of Ni only occurs with ionic Ni-species i.e., Ni-hydroxide, the catalyst should be more stable when either the Ni-hydroxide cannot be formed or when the formed Ni-hydroxide cannot dissolve. Thermodynamically the latter can be achieved at higher pH. Indeed Fig. 9 shows that the Ni particles are more stable in H_2 compared to Ar and even more stable when KOH was added to the reaction mixture. The figure shows the hydrogen chemisorption capacity of the fresh catalysts (Fig. 9 left) together with that of the used

Table 3
Capture properties of K_2CO_3 on carbon black. The weightloading was changed to change the particle size. Reproduced with permission [29]].

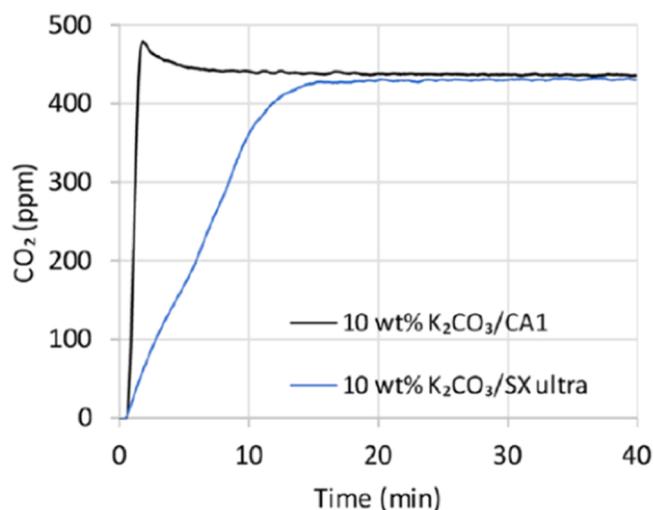| Loading (wt%)	Time of capture (min)	Efficiency (mol CO_2/mol K_2CO_3)	Particle diameter (nm)	Penetration depth (nm)
10	40	0.5	120	10
25	140	0.4	230	20
50	335	0.4	1000	80

Fig. 8. Condition 50 mg sorbent, pre-treatment RT to 200 °C: 10 °C/min, dwell time 30 min under flow of dry N_2 (100 mL/min), sorption at 60 °C for 60 min, flow of air (100 mL/min, 430 ppm CO_2, 3 vol% H_2O). Breakthrough curves for K_2CO_3 on CA1 and SX reproduced with permission from [30].

catalysts (230 °C, 6 h, 1% ethyleneglycol in water). Clearly in Ar or H_2 the hydrogen chemisorption capacity is severely suppressed after reaction indicating severe loss of Ni surface area. When using KOH containing solutions the Ni hydrogen chemisorption capacity was less suppressed thus the Ni surface area was better retained after reaction. This is supported by XRD measurements (Fig. 9 right) i.e. when using KOH solutions as reaction medium the Scherrer crystallite size is close to that of the fresh samples while samples used in Ar or H_2 without KOH showed a significant increase in crystallite size. Fig. 9 also shows that using reducing conditions (H_2 vs Ar) stabilizes the Ni though at a lesser extent as KOH did. It must be noted that a change in reaction conditions also leads to a change in selectivity i.e. in the presence of a base the yield of oxygenates is higher while at lower pH more H_2 is formed [12–15].

Since the 70-ies of the last century it is known that Mo-carbides and W-carbides show noble metal like properties [31]. Since then these carbides have been used for a number of reactions like hydrogenations, hydrodeoxygenation, hydrodesulphurization, hydrodenitrogenation and isomerizations [32–35]. We have shown that these carbides can also be active for deoxygenation reactions of lipid based feedstocks [36–39] and lignin model compounds [40]. The performance of these catalysts depends on the oxidation state of the carbides. For W-carbide we have shown that the oxides can perform decarboxylation/decarbonylation of stearic acid while the carbide is active for hydrodeoxygenation (Fig. 10).
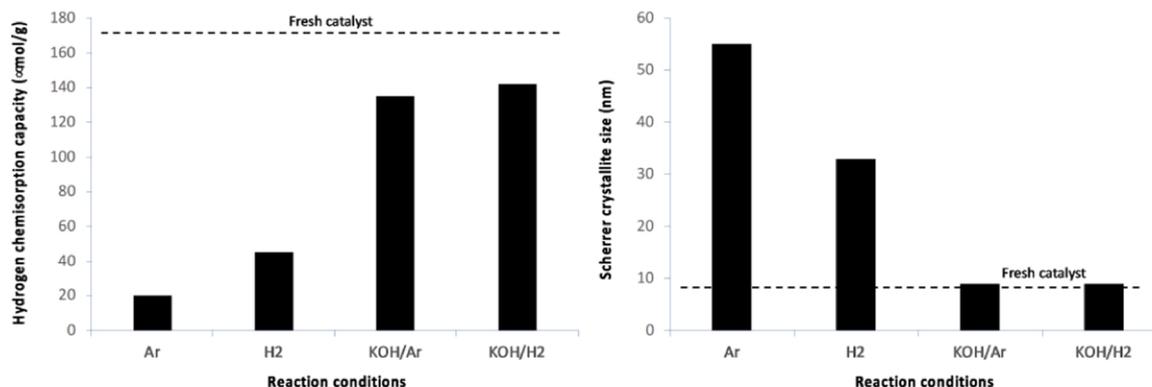
It must be noted that these conclusions were made mainly based on XRD. It is also known that the detailed surface chemistry of these carbides, i.e., the presence of oxycarbides might significantly influence the catalytic performance of these materials as well [32,35]. These carbides do offer a potential advantage for biomass conversions as well. Their stability needs to be investigated [41] but the carbides can transform to nitrides and sulfides under reaction conditions. These phases are also expected to have relevant catalytic performances [42] yet that needs to be proven under real reaction conditions.

7. Concluding remarks and outlook

Understanding support and particle size effects will remain essential for future catalyst development. To prevent a too complex catalytic system to start with carbon supports are interesting since they are inert. They are also stable under the reaction conditions needed for biomass conversion. Therefore, these supports are well suited for fundamental studies using these new feedstocks. In addition, carbon is conductive therefore electrochemical conversions can be well studied as well. Both are exemplified by the study of particle size effects in chemical and electrochemical glucose oxidation as described above.

Carbon nanofibers might be a good choice for fundamental studies due to their graphitic mesoporous nature with a high surface area. Their industrial application is not directly eminent due to their high costs. Yet the knowledge obtained with these carbon materials can be transferred to other supports.

For the use of carbon materials for fundamental studies one must keep in mind one drawback. These materials, especially the graphic high surface area materials, adsorb very effectively photons from the UV to IR range. Therefore, vibrational spectroscopy is cumbersome i.e., signal to noise ratios are very poor if a signal can be observed at all. Nevertheless cited examples show that carbon materials (dark materials) have a bright future for catalyst development using emerging feedstocks and new energy inputs.

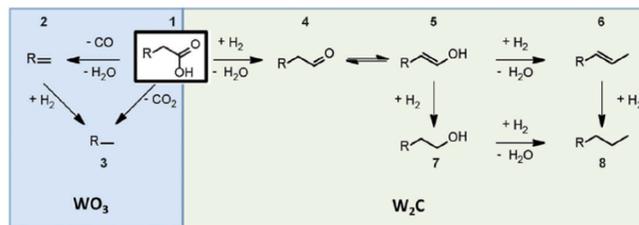**Fig. 10.** Deoxygenation pathways over WO3/CNF and W2C/CNF reproduced with permission from [36].

Fig. 9. Stability of Ni/CNF in aqueous phase processing of ethylene glycol [2 g Ni/CNF, 6 h reaction, 230 °C, 1% wt% ethylene glycol, (0.5 M KOH) batch reactor [13].

CRediT authorship contribution statement

Credit author statement for CATTOD-D-22–00331 'Dark material with a bright future: carbon as support in future heterogeneous catalysis - a short personal perspective.' By J.H. Bitter. This paper is, as explained in the introduction of the paper, a short perspective mainly based on own work. J.H. Bitter conceptualized the paper, wrote the original draft, wrote, edited and reviewed the paper. J.H. Bitter had some discussions with M. van der Ham and T. van Haasterecht who are acknowledged for that and informed on that.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

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