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REVIEW ARTICLE

Things go better with coke: the beneficial role of carbonaceous deposits in heterogeneous catalysis

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Carbonaceous or hydrocarbonaceous deposits formed on the surface of heterogeneous catalysts during reaction are typically associated with catalyst deactivation through coking. However, there are a number of cases where such deposits may enhance catalytic performance. This includes: coke deposits acting directly as the catalytically active site, *e.g.* in alkane dehyrogenation reactions; the selective deactivation of non-selective surface sites thereby increasing catalytic selectivity; and the participation of deposits in the reaction mechanism, including hydrogen and hydrocarbon transfer and the well-documented hydrocarbon pool in methanol-to-hydrocarbon conversion. The *in situ* formation of metal carbides also plays a key role in many reactions including alkyne hydrogenation and Fischer-Tropsch synthesis. These phenomena have been observed over all solid catalyst types including supported metals and metal oxides and zeolites. It is highly likely that there are many systems in which coke plays a positive role which have not yet been reported due to difficulties in deconvolving this from the role coke plays in deactivation. This review summarises the, at present disparate, literature in this important area and highlights how this understanding can be used to inform the rational design of catalysts and catalytic processes.

1 Introduction

The effects of carbonaceous deposits, or "coke", on catalyst performance have been extensively studied over the past five decades, with the principle focus on the role of coke in catalyst deactivation. There is an evident commercial need to understand the mechanisms by which coke causes catalyst deactivation, in order to optimise process efficiency. Coke deposition, however, can also have beneficial effects on catalyst performance. For instance, it can enhance the selectivity of the catalyst, *e.g.* through selective poisoning of high-energy active sites which promote undesirable side reactions. Additionally, thermal effects associated with carbon deposition may help to moderate exothermic processes and thus prevent sintering, or carbon deposits may isolate metallic particles, thus preventing sintering by geometric effects [1]. It is also becoming increasingly evident that carbon deposits can exhibit direct catalytic activity in a wide range of systems, for example in oxidative dehydrogenation, isomerisation, hydrogenation and Fischer-Tropsch reactions.

This review seeks to provide an overview of the, at present, disparate, reports on the beneficial role that coke deposits can play such that this knowledge can inform improved design of catalysts and catalytic processes. This is crucial not only in improving the sustainability of existing industrial processes, many of which rely on fossil resources, but also in developing new processes such as those utilising renewable feedstocks. A particular focus of the review is on those cases where coke has been shown, or has the potential, to play a direct role in the catalytic reaction; in particular providing active sites or reacting with adsorbed reactant species to form the desired product. Much progress has been made since the last major review of this area [2], for example, the discovery of the hydrocarbon pool mechanism in methanol-to-olefin reactions [3], and the activity of coke deposits in non-oxidative dehydrogenation reactions [4]. The catalytic activity of carbon based materials, *e.g.* activated carbons, carbon nanotubes, graphene *etc.*, has been thoroughly discussed in a number of excellent recent reviews [5–8] and hence only the catalytic behaviour of carbonaceous deposits formed *in situ* on the surface of a heterogeneous catalyst will be discussed herein.

1.1 Definition and structure of "coke"

The definition of coke is often somewhat arbitrary, and may be loosely correlated with structural parameters of the deposits. The terms young, medium and old coke have been used to describe coke in terms of decreasing hydrogen content with

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'age' or time spent on the catalyst [2,9]; whilst hard coke is distinguished from soft coke by its insolubility in chloroform or organic solvents [10]. Increasingly, advanced characterisation techniques are being used to provide quantitative information allowing coke to be described in terms of its degree of order or graphiticity [7,11]. For the purposes of this review, we will consider the role played by all carbonaceous species which are formed during reaction either on the catalyst surface or in the sub-surface region and which are not molecular products of the reaction. This therefore encompasses both deposits which are traditionally termed as "coke", but also, *e.g.*, metal carbide phases which may form *in situ*. This attests to the nature of heterogeneous catalysts as dynamic entities which evolve throughout a reaction.

The structure of carbonaceous deposits depends on the reactant, and product, species from which they derive and from the nature of the site at which they form. For instance, coke deposited from linear molecules such as butadiene may be more linear in structure than that formed from cyclic or aromatic molecules [12]. However, even from a single reactant and a single catalyst there are many different coke structures that can be formed at different temperatures; they may vary for instance in terms of their reactivity towards oxygen, hydrogen and steam [2]. Considering the influence of the active site, it is noted that cracking plays a key role in coke formation at acidic metal oxide or metal sulphide sites, while metallic sites may form coke through hydrogenolysis reactions [2,13]. Metal sites can also help to stabilise dehydrogenated carbonaceous deposits [14,15], and large metal particles are known to stimulate coke formation [16,17]. A fuller description of the proposed mechanisms of coke formation can be found elsewhere [15].

Another key factor in determining the structure of the coke formed is the reaction conditions employed. The role of temperature and pressure in determining the macrostructure of carbon deposits has been extensively studied. For example, studies of propylene pyrolysis on iron foil identified seven different macrostructures as temperature increased, from tubular whiskers around 723 K to spherical carbon particles above 823 K [2]. Studies of carbon deposits formed from steam reforming of hydrocarbons over nickel catalysts identified similar structures [18]. Of note is the finding that increasing temperatures and pressures give rise to increasingly complex and graphitic coke nanostructures. Figure 1 shows the increasingly complex structure of the carbon deposits formed from cyclohexane on HY zeolite catalysts with increasing temperature [2]. Elsewhere, in studies of carbon deposits formed from steam reforming of hydrocarbons over nickel catalysts, pyrolytic (or graphitic) carbon was identified as being formed above 873 K. Similarly, in studies of butane dehydrogenation over VO_x/Al_2O_3 catalysts, the coke deposits were found to be more graphitic in structure at reaction temperatures above 873 K, as confirmed through THz-TDS studies [11].

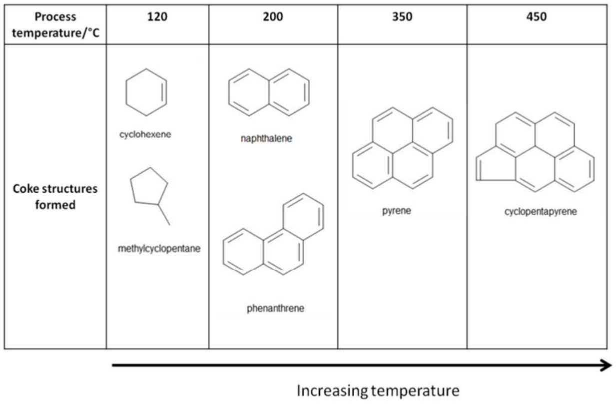

Figure 1: The influence of reaction temperature on the structure of carbon deposits formed from cyclohexane on HY zeolite catalysts. Figure produced based on data available in Menon (1990) [2].

2 Characterisation techniques

Understanding the role of carbon deposits in catalysis requires a full characterisation of the amount, composition, chemical nature and location of the coke [14]. Several techniques must be employed as no one technique can capture all of this information. Techniques vary in their ability to measure bulk or surface properties, and some may be invasive or destructive [7]. It is noteworthy that some recent studies have identified characterisation as a limiting factor, as the characterisation of catalysts did not reveal any differences that would explain the higher selectivity or activity of one catalyst over another [19–21]. The importance of using a wide range of characterisation methods, ideally conducted simultaneously on the same sample, cannot be overstated.

The most common methods used in the surface characterisation of coke can be broadly categorised as described below. Only brief details are provided here; a number of excellent reviews of catalyst characterisation techniques exist in the literature which provide greater detail [22,23].

Vibrational spectroscopy

Vibrational spectroscopy techniques analyse the interactions between photons or particles with a surface and the resulting excitation or de-excitation. This category of technique includes infrared (IR) spectroscopy, Raman spectroscopy, THz-time domain spectroscopy (THz-TDS), ultraviolet-visible (UV-Vis) spectroscopy and inelastic neutron scattering (INS). Additionally, electron energy loss spectroscopy (EELS) is also considered a vibrational technique; this is typically carried out in conjunction with transmission electron microscopy (TEM).

IR spectroscopy can be used to identify the functional groups present in a sample, as these moieties will absorb IR radiation and produce a characteristic spectrum. However, this technique is only of limited use in the study of carbon deposits, due to the highly absorbing nature of coked catalyst samples which are often black in colour. Additionally, in the case of supported catalysts, strong absorptions from the support may obscure key features in the spectrum of adsorbed species. It is therefore important to also employ methods which can probe optically opaque samples.

Raman spectroscopy is of particular relevance in the study of coke, as the Raman scattering effect is dependent on the polarisability of the species, and thus can be used to indicate the degree of graphiticity of a carbon network [7,24,25].

Terahertz-time domain spectroscopy (THz-TDS) can also provide quantitative information on the degree of graphiticity in coke samples [11,26,27]. Compared to IR and Raman spectroscopy, THz-TDS probes a lower energy region of the electromagnetic spectrum and is hence ideally suited to characterising low energy modes in extended graphitic-like networks.

UV-Vis spectroscopy has found many applications in the study of coke deposits. Typical functionalities which can be identified by UV-Vis spectroscopy include conjugated double bonds, aromatics, and unsaturated carbenium cations [28], all of which are relevant to the study of coke deposits. Studies utilising UV-Vis have identified polycyclic aromatics such as polymethylanthracenes, dienylic and trienylic carbenium ions, dienes and polyalkylaromatics [28,29]. UV-Vis has also been used to detect an overlayer containing alkenyl carbenium ions on HY-FAU zeolites as a result of hydrocarbon adsorption [30].

Inelastic neutron scattering (INS) is an emerging technology in this field and can be applied to a range of materials. Due to the high neutron scattering cross-section of hydrogen it is particularly suited for analysing hydrogen-rich coke deposits. As with Raman spectroscopy, it is also able to probe optically absorbing samples [31]. INS can provide information on how hydrogen is incorporated in a catalyst, which has applications in studying the role of hydrocarbonaceous deposits in catalysis, for example, in how they may facilitate hydrogen transfer. It has already been used in studies of hydrogen pre-treatment of catalysts [32] and hydrogen retention in catalysts [33].

Thermal methods

Thermal methods involve heating the sample under a controlled atmosphere and either monitoring the species desorbed, for example by mass spectrometry, or monitoring the mass change of the sample. Among the most commonly utilised thermal methods in coke analysis is temperature programmed oxidation (TPO), which can yield information on the coke type and location on the catalysts; peaks obtained at different temperatures correlate to different coke structures [34–37]. Temperature programmed desorption (TPD) can yield information on the functional groups present on the surface of the carbonaceous deposit [38,39], such as carboxylic acids, lactones and quinones. Other variations on the above techniques include temperature programmed hydrogenation (TPH) and temperature programmed reduction (TPR).

Thermogravimetric analysis (TGA) is also widely used to quantify the amount of coke on a surface [40,41], and to characterise the composition of carbonaceous materials in terms of their fixed carbon content, moisture, ash content and volatile components [42].

Mass spectrometry methods

Mass spectrometry methods, such as secondary ion mass spectrometry (SIMS), can be used to analyse the deposits present on the surface of a used catalyst by bombarding it with energetic primary particles and measuring the mass spectra of the secondary particles emitted. When combined with ion sputtering experiments (dynamic SIMS), this results in a technique with even higher resolution and sensitivity [43] which can reveal information about the chemical species present in coke. For example, it has been used to compare the chemical species present in coked alumina with those in anthraquinone thereby highlighting the similarity in structure between coke and anthraquinone in this case [44].

Electron microscopy and scanning probe microscopy

Scanning probe microscopy methods, such as atomic force microscopy (AFM) and scanning tunnelling microscopy (STM), are valuable techniques for obtaining high resolution images of the surface topography with minimal sample preparation. They are also relatively low cost as the equipment is relatively easy to construct and operate. Both AFM and STM work as stylus-style instruments, where a sharp probe scans the surface of the sample to detect changes in the surface and generate a signal. AFM detects the interaction force between the probe and the surface, whilst STM measures the surface electron density. Although imaging individual atoms is theoretically possible using AFM, it is in practise easier to achieve higher resolution images using STM, provided the sample is conductive [43]. Scanning Electron Microscopy (SEM) produces similar results to the above, but uses a beam of focused electrons rather than a scanning probe to produce an image, and can produce maps of the position of coke on the catalyst surface [11].

Transmission Electron Microscopy (TEM) can provide even higher resolution images, theoretically down to the atomic level, although in reality due to imperfections in manufacture or sample preparation this is not achieved. This has applications in studying changes in catalyst surfaces that occur as a consequence of reaction [11]. In combination with energy dispersive X-ray spectroscopy (EDX) and Electron Energy Loss Spectroscopy (EELS) it can be used to identify the chemical elements present on a catalyst surface, producing a compositional map on top of the microscope image. EDX is particularly sensitive to heavier elements, whilst EELS is better suited to those with lower atomic numbers, particularly from carbon to the 3d transition metals; in particular, EELS data can distinguish between different forms of carbon, such as amorphous and graphitic carbon, which has clear benefits in the study of carbon deposits [45].

Electron spectroscopy methods

Electron spectroscopy methods, such as Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS), can be applied to a variety of samples. These methods are typically associated with the production of ultraviolet (UV) radiation, which may cause disadvantages such as damage to sensitive materials. In XPS, the surface is irradiated with X-rays, which causes the emission of electrons due to the excitation of core-level electrons. The kinetic energy of these electrons is related to the atomic or molecular environment of the atom of origin, and so can be used to identify the elements in the sample. This is particularly useful for quantifying the C/H ratio or degree or aromaticity in a coke sample [11,46]. The number of electrons can provide information on the concentration of the emitting atom. AES works on a similar principle, but is based on the analysis of secondary electrons emitted following irradiation of the sample, known as Auger electrons. The energy of Auger electrons is characteristic of the element from which they were emitted. These techniques can provide information up to a depth of around 10 nm for atoms with a concentration greater than 1 mol% and can therefore, *e.g.*, yield approximate elemental surface compositions and oxidation states [43].

Developments have been made recently in "high pressure" XPS, which enables XPS of catalyst surfaces to be carried out under reaction conditions *i.e.* in a gaseous atmosphere rather than under high vacuum [47]. This technique has already been applied to studies of metal surface oxidation at mbar pressures to study oxidation states, oxide layer formation and kinetics [48–51]. Applications of the technique in catalytic studies include CO oxidation on Pt/ceria catalysts [52], catalytic oxidation of propane over nickel catalysts [53] and the role of hydrogen pressure in the deactivation of platinum catalysts [54].

Ion scattering methods

The operating principle behind ion scattering methods is that the collision of an ion with a solid surface can provide information on the atomic masses on the surface (*e.g.* the amount of coke deposited) by measuring the spectra produced as a result of the impact. As these impacts happen on a faster timescale than thermal vibrations or collision cascades, the results are considered as indicative of the instantaneous condition of the surface. Examples include low-energy ion scattering (LEIS) or ion scattering spectroscopy (ISS), which uses low energy ions to gain information on the first and sometimes second and third atomic layers. Medium energy ion scattering (MEIS) and Rutherford backscattering (RBS) are examples of higher energy methods which provide information on deeper atomic layers [43].

Interference (diffraction) techniques

Interference or diffraction methods, such as X-ray diffraction (XRD) or neutron diffraction, are used to study the geometry and symmetry of a surface. A beam of X-rays or neutrons is incident on the sample, and the intensities of the diffracted beams are studied to give an indication of bulk structure. The method can be adapted to give information on the surface structure, such as symmetry and atom coordination number.

Since this method relies on the study of diffraction patterns, it is only suitable for the study of materials with long-range order which can produce such diffraction patterns – it is therefore unsuitable for materials which are polycrystalline or amorphous, *e.g.* glasses or gels [43], but can have applications in the study of ordered coke deposits.

Nuclear magnetic resonance (NMR) spectroscopy

NMR techniques have many applications in the study of coke deposits. Brønsted acid sites for example can be investigated using a number of techniques, such as ^{1}H, ^{2}H, ^{13}C, ^{15}N or ^{31}P NMR. ^{13}C NMR played a key role in the discovery of the hydrocarbon pool mechanism by which carbon deposits play a catalytic role in the conversion of methanol to higher hydrocarbons [22] – this process is discussed in Section 3.3.2. In particular, ^{13}C NMR spectroscopy is useful for studying the carbon structure and electronic environment of carbon, but is limited to use at relatively high coke contents, above approximately 3.5 wt% [24,55,56]. ^{27}Al NMR has also been used to study changes in the aluminium chemical environment in zeolites due to coke deposition [57].

^{129}Xe and ^{131}Xe isotopes also find applications in the study of coke deposits. These isotopes are particularly sensitive probes of their local chemical environment due to their large electron cloud, resulting in a large chemical shift range, and provide a solution to the problem of the inherently low sensitivity of most NMR techniques. They have for example been used in studies of coke formation inside zeolite cages [58].

Other techniques

A variety of additional methods are employed in the characterisation of coke deposits. Chemical methods such as Boehm titration are common for detecting the presence of acidic functional groups on the surface [7,59]. Electron paramagnetic resonance (EPR), also known as electron spin resonance (ESR), spectroscopy can give information on the electronic structure and symmetry of a paramagnetic centre. It has therefore been used to study paramagnetism in coke samples (see section 3.2.1). Various elemental analysers are also available for measuring the elemental composition of a carbon sample, for example, the C:H ratio.

Combined techniques

The area of combined techniques is a rapidly developing field. No one individual technique is sufficient to provide all of the information required in order to understand how, for example, surface structure affects chemical reactivity. Demonstrated combinations of analytical techniques include NMR-UV-Vis, UV-Vis-Raman, FTIR-Raman and Raman-XRD [22]. Additionally, a combined NMR/Raman set-up has recently been developed and applied to the study of catalytic metathesis [60].The application of combined techniques allows coherent and complementary data sets to be obtained under the same reaction conditions and allow connections between two (or more) different sets of data to be drawn with much more confidence. It must be noted however that by combining techniques, a compromise is often required between, (i) the quality of one or more of the data sets, and (ii) the benefits of combined data sets.

3 The beneficial role of coke in catalysis

The beneficial role played by coke in heterogeneous catalytic reactions can take a variety of forms. Coke deposits may for instance enhance selectivity, either through improving the shape selectivity of zeolite pores or through selective poisoning of non-selective active sites; or the coke itself may be catalytically active, forming new active sites *in situ* for the reaction. The coke may instead facilitate hydrogen or hydrocarbon transfer or act as an intermediate in a variety of reactions. The various beneficial roles that coke deposits can play in a range of reactions are described below.

3.1 Enhancing selectivity through coke deposition

It is now well-established that coke deposits can lead to enhanced selectivity of products in a variety of reactions. A particularly well-studied example is the selectivation of HZSM-5 zeolites by pre-coking, particularly for isomerisation reactions such as xylene isomerisation [61,62]. Reduced yields of undesired side products such as toluene and trimethylbenzene are obtained as a consequence of the formation of carbon deposits on non-selective acid sites which would otherwise promote undesired side-reactions such as transalkylation. There may also be shape selectivation effects due to pore narrowing and steric hindrance caused by the carbon deposits [63]. Coke deposits have also been proposed to act directly as the catalytically active sites in isomerisation reactions. This is discussed in Section 3.3.3.

Pre-coking to improve selectivity in toluene disproportionation has been practiced industrially by ExxonMobil since the early 1990s through its Mobil selective toluene disproportionation process (MSTDP^{TM}), where the catalyst is pre-coked with aromatic feedstocks at elevated temperature during the initial stages of the treatment; and subsequently through its PxMax processes [62,64,65]. Figure 2 demonstrates how the pre-coking process reduces the yield of side-products over an HZ20 zeolite catalyst.

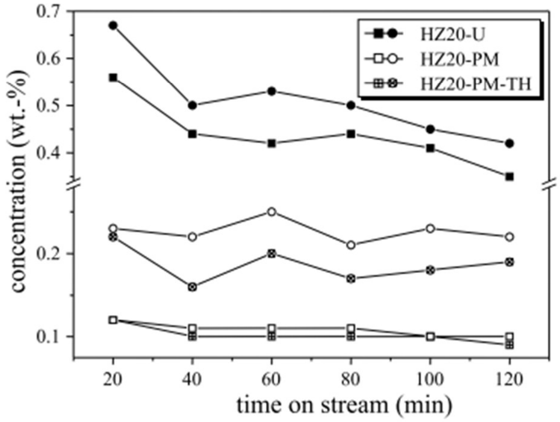

Figure 2: Yields of by-products (squares = toluene; circles = trimethylbenzenes) for unmodified (HZ20-U), pre-coked (HZ20-PM) and hydrogen-treated (HZ20-PM-TH) catalysts in xylene isomerisation at 673 K. Lower concentrations of by-products result in improved selectivity to *p*-xylene [62]. Reproduced with permission. Copyright 2001 Elsevier.

Fang and co-workers developed a five-stage reaction mechanism to explain how coke deposited during toluene disproportionation reactions led to an increase in *p*-xylene selectivity. This was attributed to the formation of coke on external catalytic sites on the zeolite, as in the initial stages of the reaction, coke was preferentially deposited on Brønsted acid sites in the channels, but no increase in selectivity was observed. This external coke modifies the surface acid properties of the zeolite, thus preventing secondary isomerisation reactions, leading to an increase in selectivity to *p*-xylene [66]. Similarly, the selectivity to *p*-xylene in toluene methylation reactions over ZSM-5 can also be increased through pre-coking of the zeolite [67]. This improvement is assigned to improved shape selectivity and deactivation of non-selective acidic sites.

The beneficial effects of coke on zeolite catalysts have also been demonstrated in ethylbenzene disproportionation, where coke is reported to be useful as a modifying agent for selectivation over H-ZSM-5 [41]. Pre-coking is also reported to improve selectivity towards benzene in the transalkylation of heavy aromatics. This however only occurs when pre-coking takes place in a hydrogen (rather than helium) atmosphere [68]. Elsewhere, pre-coking has been successfully applied to the isomerisation of *n*-butene [69–71] over ferrierite catalysts. In this case, coke blocks the porous channels suppressing dimerization reactions.

It is not only on zeolites where pre-coking, and coke deposits laid down *in situ*, can improve selectivity. Ethylbenzene dehydrogenation to styrene over CrO_x/Al_2O_3 catalysts has recently been shown to proceed through a non-selective cracking regime prior to the dehydrogenation regime [27]. Coke deposition during the cracking period was speculated to decrease the catalyst acidity and to effect a reduction in chromium oxidation state thereby diminishing the competition between acid and metal sites, hence favouring the dehydrogenation reaction. Subsequent studies demonstrated that pre-coking with aromatics improved dehydrogenation activity and suppressed cracking [72]

Coke deposits have also been linked to changes in selectivity in hydrogenation reactions*, e.g.* of pentenenitrile over supported nickel catalysts [73,74]. Additionally, the selective hydrogenation of alkynes to alkenes, which has important industrial applications, is also strongly influenced by carbon deposited during reaction. Over palladium catalysts, sub-surface carbon derived from the reactant acts to reduce over-hydrogenation of the alkene to the alkane [75]. This is discussed more fully in Section 3.3.1.

3.2 "Active coke" on catalyst surfaces

The earliest unambiguous demonstration of the ability of coke to provide catalytically active sites dates from the 1970s; namely the observation of the activity of carbonaceous deposits in the oxidative dehydrogenation (ODH) of ethylbenzene (EB) to styrene [76]. Since that time, further research has also identified the potential of coke deposits to catalyse non-oxidative dehydrogenation, while ammoxidation reactions on alumina were shown to proceed only when a certain amount of carbon had accumulated on the otherwise inert support [77].

It is however not surprising that coke deposits can directly catalyse reactions. The catalytic activity of unsupported carbon is well established, with carbonaceous materials known to catalyse a wide range of reactions, including oxidative dehydrogenation, alcohol dehydration, SO_x oxidation, NO_x reduction, catalytic wet air oxidation, halogenations and dehalogenation, decompositions of hydrazines and esterification of organic acids [7]. It is therefore very likely that coke deposits may play an important role in reactions beyond those described here.

3.2.1 Dehydrogenation and oxidative dehydrogenation

The dehydrogenation of light alkanes is important in the chemical industry for the production of unsaturated hydrocarbons which are valuable as feedstocks for the production of other chemicals, such as plastics and polymers. The typical reaction temperature of this process is in excess of 873 K. As an endothermic process, it is however very energy intensive, while the high temperatures also contribute to deactivation of the catalyst. Oxidative dehydrogenation has therefore been investigated as an exothermic process that can be carried out at lower temperatures of around 623 K. The role of coke deposits in both oxidative and non-oxidative dehydrogenation will now be discussed in more detail.

Oxidative dehydrogenation

The first observation of the catalytic activity of coke deposits was in the oxidative dehydrogenation (ODH) of ethylbenzene (EB) to styrene. It was noted that carbon deposits did not cause deactivation even after extended times on stream [78,79]. Subsequent studies by Kim and Weller showed that there was no loss of BET surface area or activity over 20 hours, even though coke was continually deposited, reaching levels of 12-13 wt% [80]. The conclusion that activity was due to the deposited carbonaceous material was subsequently reinforced by the demonstration that activated carbon and carbon fibres are active catalysts for this reaction [81–91].

The mechanism by which coke, and unsupported carbon catalysts, catalyse EB ODH has been extensively investigated. Coke deposits reduce the acidity of the alumina catalyst, which is thought to be beneficial for dehydrogenation activity [27]. However, it has also been shown that ethylbenzene reacts with quinolinic oxygen functionalities formed on the carbon surface to produce styrene. The reduced surface is then re-oxidised by gas phase oxygen or another oxidant [12]. This area has been the subject of several reviews [92–94], and methods of exploiting the role of coke in this reaction continue to be the focus of several contemporary studies [19,95].

Carbon deposits may also play a role in catalysing the ODH of *n*-butane, as these reactions have been shown to be catalysed by coals, where the reaction selectivity is increased as the coal rank is increased, although the overall butane conversion is decreased [96]. Many other oxidative dehydrogenation reactions have been shown to be catalysed by carbonaceous materials employed directly as catalysts. A number of examples are discussed in a detailed review by Qi and Su including the carbon nanotube-catalysed conversions of ethane to ethene, propane to propene, butane to butene, butane to butadiene, ethanol to acetaldehyde and 9,10-dihydroanthracene to anthracene [97]. Other catalytically active carbonaceous materials in ODH reactions include graphene oxide in the conversion of isobutane to isobutene, and amorphous carbon in the ODH of 2-butanol to 2-butanone [97]. It is therefore feasible that coke deposits may be catalytically active in these reactions.

Non-oxidative dehydrogenation

Non-oxidative dehydrogenation (DH) reactions have also been shown to be catalysed over carbon deposits. In a study by Amano and co-workers, the dehydrogenation of cyclohexane was observed to occur on a coked alumina catalyst under non-oxidative conditions, but only isomerisation reactions were observed on the pure alumina catalyst [4].

Considering the DH of *n*-butane over VO_x/Al_2O_3 catalysts, it was found that the increase in butadiene production was not concurrent with a decrease in the selectivity towards 1-butene, indicating the formation of a new catalytic site during reaction, *i.e.* carbonaceous deposits [11]. A schematic of this is shown in Figure 3. The studies also found that the coke completely encapsulated the vanadium oxide catalyst, preventing access to VO_x sites, but without deactivating the catalyst, thus providing further evidence for the catalytic role of the coke deposits. The catalytic activity of coke deposits in ODH and DH reactions was confirmed by comparing the activity of coke deposits with that of unsupported carbon nanofibres, which were also shown to be catalytically active [11,19].

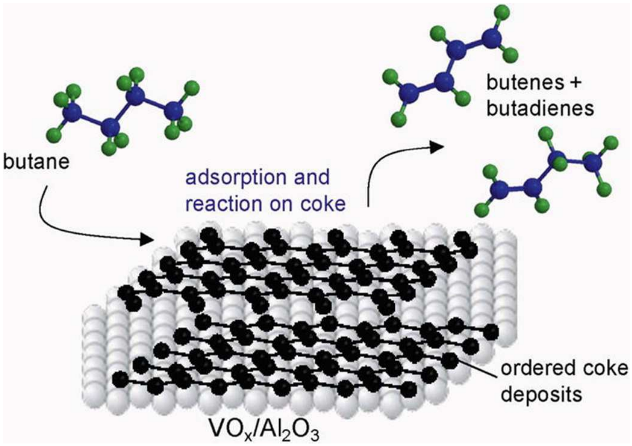

Figure 3: Coke deposits on VO_x/Al_2O_3 provide the catalytically active sites for *n*-butane dehydrogenation at 973 K. Reproduced with permission [11]. Copyright 2010 Elsevier Inc.

Nature of active sites

Some studies on oxidative dehydrogenation reactions concluded that the active sites for such reactions over coked catalysts are oxygen-containing surface groups, such as quinones or hydroxyls [44,78,85,86,92,93,98]. However, studies of the catalytic activity of carbon deposits in dehydrogenation reactions under non-oxidative atmospheres showed that they exhibit very similar behaviour (albeit at a higher temperature than ODH), although no oxygen is present in the coke deposits [19]. In the latter case at least, it is therefore likely that defects in the coke structure form the active sites.

The formation of these defects may include the breaking of carbon-carbon bonds in otherwise ordered carbon deposits, and thus the presence of unpaired electrons, or paramagnetism. The degree of paramagnetism has been linked to the catalytic activity of coke samples using EPR, thereby suggesting they may act as the active sites [11,78,84,92]. Similar behaviour was also found on zirconia catalysts, on which the active site had previously been identified as tetragonal phase zirconia. However, carbon deposition was a common feature which better explained the similarities in dehydrogenation behaviour [99]. Further experimental and theoretical investigations are required in order to definitively identify the role of defects and paramagnetism in the catalytic activity of coke deposits.

Role of graphitic structure

Catalytic activity in non-oxidative dehydrogenation also appears to be related to the structure of the coke deposits formed, with several studies finding that increased graphitic order in carbon deposits correlates with increased catalytic activity [11,37]. The extent of graphitisation required in order to exhibit this activity is however unclear, although terahertz spectroscopy studies by McGregor *et al.* indicated that it was likely to require more than 7 aromatic rings [11]. Carbon deposits shown to be active in non-oxidative cyclohexene dehydrogenation were also characterised as having a graphite-like structure [4]. Considering ODH, studies on coal samples in the ODH of *n*-butane also found increased selectivity to butane with increased graphiticity, although a lower overall conversion was achieved [96].

3.2.2 Ammoxidation

Ammoxidation is the reaction of *e.g.* carbons with a mixture of ammonia and air, typically at temperatures between 523 and 673 K [100]. Carbonaceous deposits formed in alumina pores have been shown to be catalytically active for the ammoxidation of ethylbenzene [77] and toluene [101]. Alumina is inactive until a certain quantity of carbon has accumulated on the acid sites of the inert support; the carbon deposits then provide active sites in a similar manner to dehydrogenation reactions (section 3.2.1), with catalytic activity again correlated with the concentration of carbon radicals, *i.e.* the degree of paramagnetism [101]. It has been noted both in ammoxidation reactions and elsewhere that nitrogen-containing coke can be more catalytically active than that which does not contain nitrogen. For example, in the ODH of ethylbenzene with nitrobenzene, the use of nitrogen-containing cokes (produced using nitrobenzene and aniline) resulted in a higher conversion than coke which contained negligible nitrogen [77]. The structure and role of nitrogen moieties in catalytic carbons has previously been the subject of in-depth characterisation [26]. Elsewhere, the inclusion of heteroatoms such as nitrogen have been shown to improve the performance of graphene in a range of catalytic applications [8].

3.3 Hydrogen and Hydrocarbon Transfer

Reactions involving hydrogen and hydrocarbon transfer are widely used in the chemical industries to produce a variety of chemicals. Hydrogen transfer reactions may include hydrogenation and dehydrogenation, whilst hydrocarbon transfer reactions are important for the conversion of hydrocarbons to other chemicals, for example methanol-to-olefin reactions. These types of reactions are widely studied and the roles of carbon deposits in facilitating and catalysing these reactions are increasingly well understood, and are discussed further below.

3.3.1 Hydrogen transfer reactions

Carbonaceous deposits can facilitate hydrogen transfer in both alkene hydrogenation and catalytic cracking reactions, in addition to effecting the reduction of a catalytic metal site. In processes such as coal liquefaction, both hydrogenation and cracking reactions are involved [102]. Thomson and Webb were among the first to suggest that the hydrogenation of alkenes on metals may not be the result of direct addition of hydrogen from the gas phase to the adsorbed alkene, but instead a hydrogen transfer reaction between an adsorbed hydrocarbon and the adsorbed alkene [103]. This mechanism may be behind the reported insensitivity of some alkene hydrogenation reactions to the nature of the metal used [103,104].

Hydrogen transfer from adsorbed carbon species also has analogies to liquid-phase hydrogenation systems where hydrogen-donating solvents such as tetralin are employed. The hydrogen-donating ability of tetralin is due to the hydrogens in the saturated ring being activated by the adjacent aromatic ring. This leads to a reduction in non-selective coke formation in hydrogenation and cracking reactions, as the tetralin donates hydrogens to satisfy the supply of free radicals formed [102,105]. It has been suggested that the hydrogen carrier is the ethylidine radical [106]. Upon hydrogen-transfer, tetralin is dehydrogenated to naphthalene, which is then rehydrogenated to tetralin by the gaseous hydrogen supplied, usually in the presence of a palladium catalyst [107]. As aromatic rings are a common feature of coke molecules, it is likely that aromatic coke molecules can act as hydrogen-donors in a similar manner to the more established mechanism involving aliphatic carbon deposits.

The nature of the coke precursor plays an important role in determining the influence of coke deposits on reaction. For example, carbonaceous deposits from *cis*-2-pentene were shown to activate the hydrogenation reactions of *trans*-2-pentene to *n*-pentane, and *vice versa* [74]. A similar effect was found for the catalytic wet air oxidation of phenol reaction, whereby the origin of the coke had a greater influence on the subsequent phenol conversion than any surface modifications made to it [20].

3.3.2 Hydrocarbon transfer reactions

Methanol-to-hydrocarbons

Methanol-to-olefin (MTO), methanol-to-aromatics (MTA) and methanol-to-hydrocarbon (MTH) reactions – generally MTX – are of increasing industrial interest as a means to generate valuable products in the so-called “methanol economy”. Significant industrial application of this process is already established. MTX processes provide a means to form longer chained products from a C1 substrate [3]. Hydrocarbonaceous deposits play as key role in these reactions as part of the hydrocarbon pool mechanism [3,108,109].

In the hydrocarbon pool mechanism methanol is first adsorbed onto the surface of the catalyst, typically ZSM-5 or SAPO-34, where it is subsequently converted to carbonaceous deposits to form a hydrocarbon pool. This pool then plays a role in the conversion of further methanol molecules to higher hydrocarbons, which then desorb from the hydrocarbon pool as products, as indicated schematically in Figure 4. The structure of this pool is thought to be methyl-aromatic in nature (*e.g.* xylene, toluene) [110]. Figure 5 shows a detailed proposed mechanism, indicating the role that both hydrocarbon and hydrogen transfer processes play in the production of olefins. In MTO it has been observed that the activity and selectivity over a zeolite catalyst increases with coke content up to 5 wt% coke [111], correlating with the formation of the pool. It is worth noting that not all of the hydrocarbon pool is reactive or accessible, as shown in ^{13}C NMR studies [22].

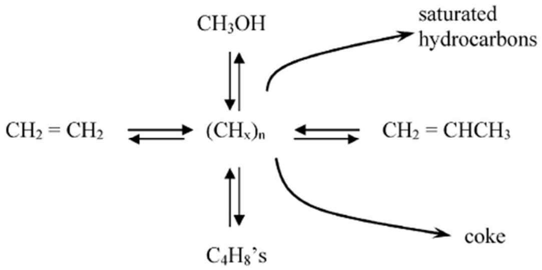

Figure 4: The hydrocarbon pool mechanism over SAPO-34, as proposed by Kolboe [108]; figure taken from [3]. Reproduced with permission. Copyright 2011 Royal Society of Chemistry.

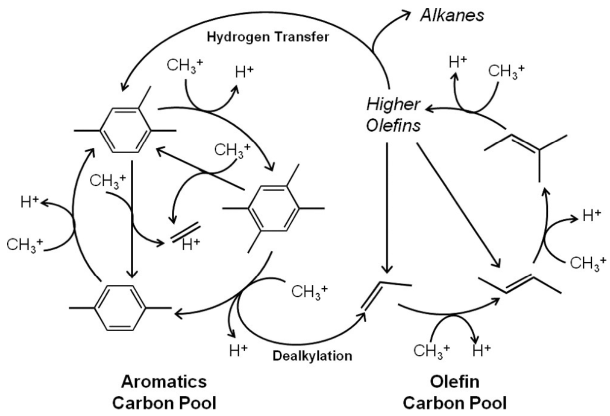

Figure 5: The hydrocarbon pool mechanism over HZSM-5 [112]. Reproduced with permission. Copyright 2013 American Chemical Society.

It has been speculated that the initial hydrocarbon pool may form as a result of trace impurities in the feed, such as aldehydes, ketones and higher alcohols, rather than from the methanol directly [113]. In one study, in the absence of a hydrocarbon pool, the conversion of methanol to hydrocarbons over a solid acid catalyst was only 0.0026%, but after three identical pulses of methanol, the conversion dramatically increased to almost 10%, indicating that the adsorbed impurities had a catalytic effect on MTX reactions [113].

Homologation

Homologation reactions are reactions in which large molecules react with smaller fragments to form the next molecule in the homologous series [114,115]. Menon proposed a two stage mechanism for methane homologation whereby CH_4 initially reacts with the catalyst to form carbidic coke, with the coke then reacting with hydrogen to form ethane [116]. The same process also applies to alkene homologation. That reactive carbon plays a role in homologation is supported by the finding that the quantity of reactive carbon formed in methane-propylene homologation correlated with the C4 yield [117]. The ease of migration of carbon from the metal to the support is thought to be responsible for the greater selectivity in these reactions, however this depends on the type of support, which determines the reactivity of the coke formed [118].

3.3.3 Pore Mouth Catalysis

Coke molecules located at pore openings (*i.e.* the pore mouth) may interact with protonic sites. These hybrid organic-inorganic sites have been proposed as selective active sites for the conversion of methanol over SAPO-34, for isomerisation reactions and for alkylation processes [119]. Examples of these are now discussed below.

Isomerisation

The skeletal isomerisation of *n*-butenes to isobutene is an important reaction as isobutene is employed in the production of MTBE (methyl tert-butyl-ether), an octane enhancer for petrol [120]. Improvements in selectivity have been documented to coincide with the formation of carbonaceous deposits [70,121–123]. While it had been proposed that this was due to modification of the pore diameter in the HFER zeolite catalysts employed [71,124–126], it was observed that high selectivities were obtained even with the pores entirely blocked [56]. It was therefore proposed that the reaction proceeds *via* the formation of carbocations from the carbon deposits, which act as the active site [122,127]. A schematic of this process is shown in Figure 6. Pore-mouth catalysis has also been implicated in the hydroisomerisation of long-chained alkanes. For example, employing platinum modified zeolite catalysts at temperatures of 453-550 K, Marten and co-workers obtained yields of branched alkenes inconsistent with a classic bifunctional reaction mechanism, implicating pore-mouth catalysis as the key step in the process [128].

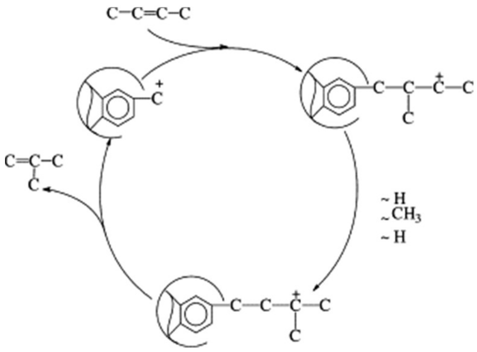

Figure 6: Schematic of the mechanism of pore mouth catalysis. Reproduced with permission [119]. Copyright 2002 Elsevier.

Alkylation

Pore mouth catalysis is also believed to play a role in alkylation reactions, such as the alkylation of toluene and the isopropylation of naphthalene. The former reaction is of commercial interest as the product, *p*-xylene, is an important precursor for the production of polyester fibres. Da and co-workers investigated the alkylation of toluene with 1-heptene at 363 K, observing that the concentration of bi- and tri-alkylated toluene molecules trapped within the pores decreased over time, even after total consumption of 1-heptene had occurred, as a result of the transalkylation with toluene at the pore mouth [129]. This also suggests a mechanism whereby catalysts which have been deactivated through pore blockage can be regenerated through treatment with toluene, thereby removing trapped molecules *via* this same process. The isopropylation of naphthalene over HFAU and HBEA zeolites shows an increase in conversion with time, despite a rapid decrease in the micropore volume of the catalysts accessible to nitrogen to a negligible value. This is consistent with the involvement in the reaction mechanism of alkylated naphthalenic species trapped at the pore mouth [119]. Another study identified pore mouth catalysis as the mechanism of alkylation of naphthalene and toluene [130].

Coke has also been observed to cause the alkylation of *p*-xylene in FCC catalysts through TEOM studies. In the absence of coke, no reaction was observed. It was also observed that acidic sites were necessary for this process, as when the sites were neutralised with quinoline, no alkylation activity was observed [131]. This indicates that coke deposits can be catalytically active in alkylation reactions, and appear to facilitate alkylation in the presence of acidic sites.

3.4 *In situ* Carbide formation

Increasingly, studies are investigating the role that metal carbides may play in catalysing reactions. In addition to their application as catalysts directly, metal carbides can also be formed *in situ* from the reaction of hydrocarbons with metal atoms, and may form in a wide range of reactions. It is therefore important to understand their effects on catalytic processes.

3.4.1 Selective alkyne hydrogenation over PdC_x

Selective hydrogenation of alkynes is a particularly important process for improving the quality of alkene streams, particularly the removal of acetylene impurities in ethylene feeds [132], and to prevent the poisoning of polymerisation catalysts by alkynes [133]. A particularly noteworthy example of catalytically active carbides and related species is the formation of a PdC_x phase, which has been shown to enhance the selectivity of alkyne hydrogenation towards alkenes. The selectivity of non-promoted palladium to alkenes is fairly low (*e.g.* selectivity to propene is less than 20% when the H_2:propylene ratio is greater than 2 [132]), but the formation of carbide phases leads to an increase in alkene selectivity by destabilising alkenes adsorbed on the surface (*i.e.* it desorbs before further hydrogenation can occur), and by inhibiting the formation of the high energy, unselective, sub-surface hydrogen that promotes over-hydrogenation [132–134]. Smaller palladium particles reduce the amount of coke formed, and thus inhibit the formation of the PdC_x phase, leading to a decrease in selectivity of reaction towards alkenes [135]. Other experimental studies observed that less carbon was dissolved in the palladium catalyst during unselective hydrogenation as compared with selective hydrogenation [75].

DFT studies have confirmed this hypothesis, for example, one study found that the formation of subsurface carbides and hydrides improves selectivity of acetylene hydrogenation by weakening the surface-adsorbate bond [136], and recently published work by Yang and co-workers has also concluded that a carbide phase forms the catalytically active phase in the selective hydrogenation of acetylene through studies of Pd(100) and Pd(111) [137]. Kitchin and co-workers also found that the formation of a metal carbide phase inhibits the formation of non-selective sub-surface hydrogen in other early transition metals, implying that this may be relevant to alkyne hydrogenation over catalysts besides palladium [138]. A schematic of the palladium surface structure can be seen in Figure 7.

Particular examples of reactions where the PdC_x phase has been shown to improve catalytic performance include the selective hydrogenation of butadiene [139], propyne [132] and 1-pentyne [75,134,140,141]. This phase has also been shown to form during the decomposition of acetylene [142] and the acetoxylation of ethylene [143]. The mechanism of the formation of the PdC_x phase is still being studied, but is thought to involve hydrocarbon fragmentation to form atomic carbon, which penetrates the palladium lattice and prevents the formation of a sub-surface hydride phase [134,141]. Heating the lattice leads to a decrease in catalytic activity, suggesting that the phase is only metastable [134].

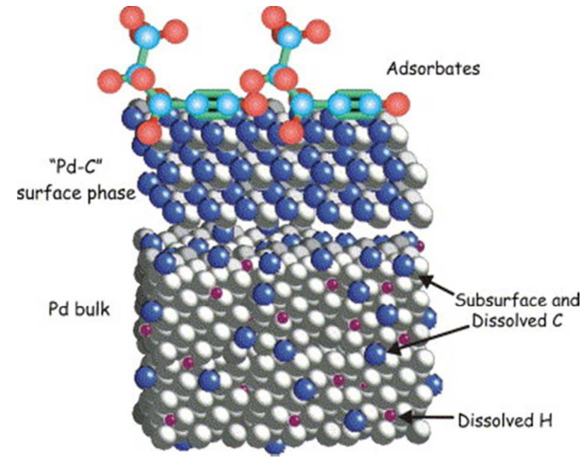

Figure 7: Model of the palladium surface demonstrating the role of the palladium carbide phase during 1-pentyne hydrogenation [134]. Reproduced with permission. Copyright 2006 Elsevier.

3.4.2 Fischer-Tropsch synthesis and CO methanation

Fischer-Tropsch (FT) synthesis is the processes whereby carbon monoxide and hydrogen are converted into a variety of hydrocarbonaceous products, most commonly on ruthenium, iron and cobalt catalysts [144]. FT reactions were noted to be 'coke-insensitive' by Menon, meaning that the deposition of coke did not lead to a decrease in catalytic activity [2]. The formation of carbon deposits could also have beneficial effects, such as preventing the formation of metal carbonyls and their subsequent volatilisation, which can lead to as much as 40 wt% loss of the metal [145].

There is a general consensus in the literature that whilst graphitic carbon can deactivate the catalyst used in FT synthesis, carbidic carbon formed *in situ* on iron catalysts may act as an intermediate [2,146]. Studies employing isotopically labelled carbidic carbon noted that the ^{13}C was contained mostly in the methane, rather than in higher hydrocarbons, directly implicating carbides in the methanation reaction; itself an important process as well as a side-reaction in FT [147]. Additionally, a reactive carbonaceous pool has been proposed as part of the mechanism for the synthesis of aromatics from FT [2].

The role of carbides is dependent upon the metal employed; it is generally accepted that iron carbide, rather than metallic iron, is the stable and active phase in ferrous catalysts, although the particular form which is responsible for the activity is still a matter of debate [148,149]. Cobalt carbides however are inactive in FT synthesis [150], and the formation of carbon deposits and carbides on cobalt catalysts contributes to their deactivation [151,152].

Iron carbide nanoparticles may also act as active sites for the chemisorption of CO to form monomers for polymerisation, leading to the formation of higher hydrocarbons [153–158].

Methanation may also be more likely to occur at iron carbide sites, whereas lower olefins may be produced at terraced sites promoted by alkali metals [159]. The factors affecting catalyst performance in FT synthesis are the subject of a recent review, and further developments in catalysts for Fischer-Tropsch synthesis can be found therein [144]. While CO is typically the carbon source in FT and methanation reactions, increasingly CO_2 is being employed as a feedstock in these processes, with a view to utilising gas captured from point sources. The reaction mechanism for CO_2 involves breakdown to CO [160], hence carbides will play the same role in these processes as they do for conventional CO reactions.

3.4.3 Molybdenum oxycarbides

The catalytically active molybdenum oxycarbide has been shown to improve selectivities in isomerisation of *n*-heptanes and higher hydrocarbons, a significant advancement over other studies which claimed that this could not be performed selectively over acid catalysts without excessive side-product formation due to cracking [161]. The carbon atoms are thought to fill some of the vacancies in the molybdenum oxide phase, stabilising the phase and leading to the formation of a catalytically active carbide phase *in situ*. Ledoux *et al*. proposed a bond-shift mechanism for the selective isomerisation [161]. The same oxycarbide phase has also been demonstrated to be selective for the dehydrogenation of short-chain alkanes.

3.5 Other reactions

Coke has the potential to be catalytically active in other reactions as indicated by the wide application of carbon based catalysts. This section introduces a number of systems where coke is known to, or may, play a key role; although in some cases further mechanistic investigations may be required in order to elucidate the true reaction mechanism.

3.5.1 Oxidative coupling

Oxidative coupling is used to produce a variety of important chemicals, such as imines for the synthesis of nitrogen-containing compounds for the biological and pharmaceutical fields [162], while the oxidative coupling of methane (OCM) followed by oligomerisation has been proposed as a means to exploit stranded natural gas fields [163]. These reactions are typically catalysed by transition metals, but carbon-based catalysts have also found applications in this area. For example, oxidative coupling of phenol is known to occur on activated carbon catalysts, leading to the formation of phenol dimers and phenolic polymers [164]. The role of carbon, either from coke or as a catalyst, in this process is as an oxygen radical generator, causing the formation of dimers and phenolic polymers by oxidative coupling, which ultimately leads to the deactivation of the catalyst through pore blockage [20,21]. In studies of OCM over metal catalysts using ^{13}C-labelled methane it was shown that the carbon formed was a reactive intermediate in methane oligomerisation and methane-alkene coupling reactions [116,165]; coke deposits are likely to participate in a similar way. OCM continues to be a topic of contemporary interest, *e.g.* through the recent EU Framework 7 OCMOL project [166–168].

3.5.2 Metathesis

Metathesis reactions involve the exchange of bonds or substituents between two molecules. It is thought that hydrogen transfer, possibly facilitated by coke deposits, plays a role in deactivating the non-selective active sites, allowing metathesis to occur [126,169]. Metathesis catalysts such as WO_3/SiO_2 do not appear to exhibit deactivation, even at coke contents as high as 49 wt%; although the coke was deposited on the silica support rather than the tungsten in this study [40]. Other studies have found that tungsten oxide is inactive for metathesis [170,171]. If active sites are still available for the metathesis reaction at such high coke contents, it is plausible that the carbonaceous deposits are in fact providing them.

3.5.3 Reforming

Carbon deposits have also been recognised as having a positive role in hydrotreating processes. Hydrotreating involves the reduction of sulphur, nitrogen and aromatic content in crude oil refining. It is assumed that the carbon enhances the number, rather than nature, of the active sites, as there is no evidence of the carbon deposits facilitating an increase in selectivity. This leads to a reported 60% increase in catalytic activity, whilst carbon-free catalysts show a noticeable deactivation of 25% after 18 hours on stream. Pore plugging has been ruled out in this case as there was no significant change in porosity of the catalyst. Both aliphatic and aromatic carbon were detected by ^{13}C NMR, and it was suggested by the authors that the carbon deposits improved the stability of the active phase by restricting the migration of $(Co)MoS_2$ [1].

It is also noteworthy that carbon has shown beneficial properties in several studies as a support material for hydrotreating catalysts, as they are resistant to coke deposition and have a higher catalytic activity per unit mass of catalyst in comparison with traditional alumina-supported hydrotreating catalysts [172–174]. The active site however is believed to be Ni, Mo and S nanoparticles [172], but the carbon does play a chemical role by inhibiting metal-support interactions, thus improving sulfidation [175]. Aryee *et al*. report that several forms of carbon have been used as supports for hydrotreating catalysts, including activated carbon and carbon nanotubes [175]. However, it is expected that alumina will continue to be the more popular choice of catalyst support due to its higher mechanical strength and functionality versus that of activated carbon [172].

3.5.4 Reactor Wall Coking

Coke formation on reactor walls may also play a role in promoting reactions. In these cases the material out of which the reactor is constructed can have a significant effect on the reaction, as stainless steel reactors, for example, may catalyse the formation of catalytically active coke on the walls [176]. In such examples, the incorporation of metal from the reactor wall into the coke may strongly influence catalytic behaviour. However, the unrecognised participation of the reactor walls in reactions makes it difficult to determine the proportion of the reactivity coming from the catalyst as opposed to from the walls [177].

A study carried out by Gornay *et al*. aimed to determine the role of the carbon deposited on the walls in the pyrolysis of octanoic acid [178]. The reactor walls were found to catalyse coke formation, particularly reactor walls containing Fe and Ni, but it was then found that the coke deposits had an 'accelerating' effect on the pyrolysis of octanoic acid. This was attributed to the Fe and Ni metal content of the coke, which was incorporated into the coke from the reactor walls [178]; these metals are known to be catalytically active.

Note that while most industrial reactors are fabricated from metallic materials such as stainless steel, many laboratory research reactors are constructed from quartz or other glass. In these cases, while the laboratory studies provide insights into the fundamental reactions occurring on the catalyst surface they will not identify the potential role of the reactor wall, and any coke formed there, in industrial application.

Studies have also been carried out on the influence of metal impurities in carbon nanotube catalysts, as they are often prepared using supported-metal catalysts, which may remain as metallic contaminants [88]. This has been investigated by treating carbon nanotubes by refluxing in strong acid to remove metal contaminants; the quantity of residual metal was then measured by X-ray fluorescence spectroscopy. These studies confirmed that the quantity of metal was very low (around 0.1%), and that it was not present on the surface, only in the bulk. Further studies deliberately added iron to carbon nanotubes, and concluded that the selectivity to alkene conversion decreased with increasing iron content [88].

4 Implications for process development

A better understanding of the role of catalytically active coke deposits holds much potential for improving the efficiency and sustainability of catalytic processes, as well as the development of novel catalytic materials. These implications are discussed below.

Tailored materials synthesis

The deliberate exploitation of carbon deposits has promise for future catalytic process development, with the ability to tailor different carbon (nano)structures for specific purposes. Additionally, the understanding gained from these studies can in some cases inform the design of novel catalysts based on the beneficial coke structures observed. In a study on oxide/carbide transition reactions on iron surfaces, carbide particles were shown to catalyse graphitic filament growth [179]. Other studies have investigated the use of lasers to produce carbon composites with particular nanostructures, for example, incorporating metal ions to increase heat dissipation and thus enhance graphitisation of the carbon matrix [180], or functionalisation of carbon nanotubes for use as catalysts for a number of applications*, e.g.* in fuel cells [181,182].

Another method for producing materials with desired characteristics is by using surface treatments. These can be generally classified into chemical, physical and biological types. When considering chemical surface treatments, acidic treatments for example can provide materials with more hydrophilic surfaces and more acidic character, whilst basic treatments may produce catalysts well suited for adsorbing negatively-charged species in greater amounts [183].

Sustainability

Through understanding the role of carbon, the sustainability of heterogeneous catalysis can be improved in a number of ways.

Metal-based catalysts are increasingly becoming unsuitable for commercial use due to their high cost and limited reserves [8,16], and so catalysts made from carbon, either with or without metals present, may provide a more sustainable and economic alternative. This new class of carbon-based catalysts may also open up new reaction pathways utilising more sustainable raw materials instead of fossil fuels [184]. Furthermore, metal carbides are able to catalyse many reactions which currently employ rare platinum group metals (PGMs), a phenomenon ascribed to the similarity in electronic structure between carbides and PGMs [185]. Elsewhere, understanding the role of carbon may also allow carbonaceous by-products of the biomass industry, such as biochar, to find applications in heterogeneous catalysis [186], or it may aid in the catalytic conversion of biomass to useful raw materials, such as the hydrogenation of cellulose [184].

The deliberate formation of catalytically active coke could also be used to enhance activity or selectivity [74]. Improving the selectivity of reactions reduces the amount of raw material that is wasted, and also reduces the energy and economic costs needed to separate the desired products, thus improving the sustainability of the process.

5 Conclusions and Outlook

Whilst coke is perhaps best known for causing catalyst deactivation, this review has shown that coke can also play various beneficial roles in catalysis in a wide range of reactions and through a variety of mechanisms. Pre-coking of zeolites is commonly used industrially to improve the selectivity of isomerisation reactions, whilst in other processes the coke may be catalytically active and provide the active sites for reaction. This can result in increased selectivity and/or catalytic activity, depending on the process and the particular mechanism by which coke catalyses the reaction. The range of reactions known to be catalysed by structures or phases formed as a result of carbon deposition include ODH (*e.g.* ethylbenzene to styrene, butane to butene, ethanol to acetaldehyde), non-oxidative dehydrogenation, hydrogenation, ammoxidation, methanol-to-hydrocarbon reactions, homologation, isomerisation, alkylation, Fischer-Tropsch synthesis, CO methanation, oxidative coupling, metathesis and reforming.

Given that coke can be catalytically active in such a wide range of processes, it is unsurprising that the mechanisms by which it can enhance catalytic activity vary between processes, and as a result, different coke structures can be beneficial depending on the particular reaction. For example, polyaromatic coke deposits may facilitate hydrogen transfer in hydrogenation reactions, whilst the formation of a metal carbide phase has been shown to enhance the selectivity of alkyne hydrogenation. Increasingly graphitic and paramagnetic coke is thought to be particularly effective in ammoxidation and oxidative dehydrogenation reactions, where it is believed to act as the active site. The hydrocarbon pool mechanism in methanol-to-hydrocarbon reactions, whereby coke is involved in the reaction mechanism through hydrocarbon transfer reactions, is another example of the activity of carbonaceous deposits.

Active coke deposits need not form only on the catalyst surface. Coke formed on reactor walls can also play a catalytic role. In these cases some metal atoms from the reactor wall may be incorporated in the coke deposits. In other systems the inclusion of heteroatoms such as nitrogen, oxygen, boron or sulphur in carbon structures can increase catalytic activity.

Through understanding the beneficial role of coke deposits in catalysis, there are many implications for future process development. For example, it may lead to the development of nanostructures tailored for specific reactions. It could also lead to improved process sustainability; metal-based catalysts are becoming increasingly unsuitable due to their limited reserves, making carbon catalysts a more sustainable alternative. This could include the use of carbonaceous by-products such as biochar as catalysts, for example. These new catalysts may also open up more sustainable reaction routes, using more sustainable feedstocks or lower energy pathways. Increased selectivity also has clear advantages for reducing separation costs and the associated energy costs, resulting in a more sustainable and economic process.

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Things go better with coke: the beneficial role of carbonaceous deposits in heterogeneous catalysis

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Carbonaceous deposits on heterogeneous catalysts are traditionally associated with catalyst deactivation. However, they can play a beneficial role in many catalytic processes, *e.g.* dehydrogenation, hydrogenation, alkylation, isomerisation, Fischer-Tropsch, MTO *etc.* This review highlights the role and mechanism by which coke deposits can enhance catalytic performance.