

Catalysts in Syntheses of Carbon and Carbon Precursors

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Materiais de carbono têm sido aplicados em diferentes campos, devido ao seu desempenho e aplicação únicos. Naturalmente, as estruturas físicas e químicas dos precursores de carbono e materiais de carbono definem as suas propriedades e aplicações. Os catalisadores apresentam um papel importante na síntese de precursores de carbono e materiais de carbono, por controlar a química composicional e molecular na transformação de substratos orgânicos em carbono, através de intermediários carbonáceos. Um desempenho maior dos materiais de carbono pode ser obtido, a custos mais baixos, através da seleção cuidadosa de catalisadores e processos catalíticos adequados na síntese de fontes de carbono, na carbonização, ativação, grafitização, modificação de precursores de carbono e no crescimento destes materiais de carbono.

Carbon materials have been applied in different fields because of their unique performances. Naturally, the physical and chemical structures of carbon precursors and carbon materials decide their properties and applications. Catalysts play a very important role in the synthesis of carbon precursors and carbon materials by controlling the molecular and compositional chemistry at the transformation of organic substrates into carbon through carbonaceous intermediates. Carbon materials of high performance and low production cost can be realized, through carefully selecting suitable catalysts and catalytic processes in the synthesis of carbon feed, carbonization, activation, graphitization, and modification of carbon precursors, and carbon growth.

Keywords: catalyst, mesophase pitch, carbon nano fiber, activated carbon, graphitization

1. Introduction of Carbon and Carbon Chemistry

Carbon has been recognized an important group of materials and devices in the modern, as well as traditional, society for many years.¹⁻³ Its importance is enlarging still now in the 21 century, providing very unique performances in different fields such as electric and heat conductions (conductor and semi-conductor), energy storage (battery anode, super capacitor and gas storage), environmental protection (activated surface), special materials (mechanical reinforcement, high temperature), etc. Its unique performance originates from its structure, even if the carbon material consists basically of carbon element alone. Figure 1 illustrates carbon allotropes adapted from Bourrat's figure.⁴ 90% of carbon materials used in the industries are graphitic, consisting of sp² carbon in hexagonal planes, as illustrated in Figure

1. The stacking alignments of the hexagonal planes with the height from a few to several hundreds nanometers, are the basic structure of the graphitic carbon groups.

Franklin proposed a 2-dimensional structural concept on graphitic and non-graphitic carbons which are two typical examples of the sp² carbon group, as shown in Figure 2.^{4,5} Such structural concept explains the variable properties of two typical hard and soft carbons and their graphitizability which defines the graphitic extent, after their graphitization above 2500 °C. The former carbon tends to stay as poor graphite while the latter one forms excellent graphite. The alignment of cluster units is particularly emphasized to be critical on the carbon graphitizability.⁶

The Franklin concept, however, lacks two aspects, three dimensional and regional images of carbon. The first image can distinguish groups of less graphitizable carbons and the second image comes from the concept of structural hierarchy in the varieties of carbon materials, as summarized in Figure 3.

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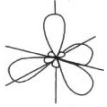
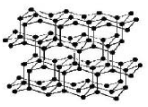
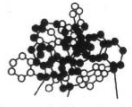
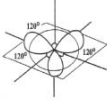




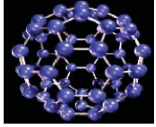
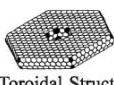
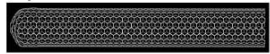

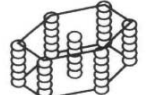
Bonding Hybridization	Allotropes	Derived and Defective Forms
 SP^3	 Cubic diamond	 Diamond-like Carbon
 SP^2	 Hexagonal graphite	Polycrystalline Graphite  Carbon Black Cokes and Activated Carbons  Pyrocarbons
 $SP^{2+\epsilon}$ rehybridization	 Fullerene	Bucky Onions  Toroidal Structures Acetylene Blacks  Nanotubes
 SP^1	 Carbyne	

Figure 1. Carbon allotropes adapted from Bourrat's figure.

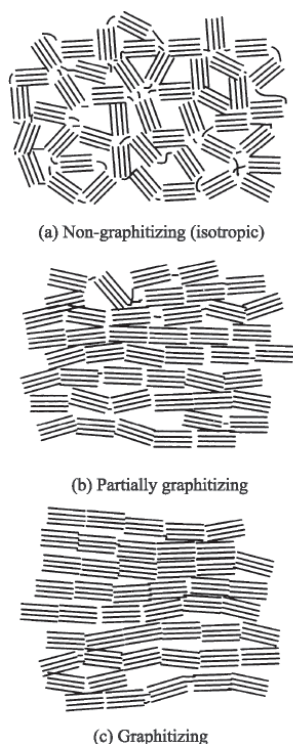
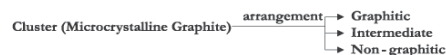


Figure 2. Franklin models for isotropic and graphitizing carbons.

Optically anisotropic units in the graphitized carbon and fibrils found by the optical microscopy in the carbon fibers are the typical examples of the assembly units in the structural hierarchy of carbon materials,⁷ as shown in Figure 4.

Franklin Model of Carbon



Angstrom- and Nano-scopic Views of Current Carbons

- Three Dimensional Arrangements : Fibers, Needle Coke, Glassy Carbon (Carbon Shape)
- Regions of Uniform Arrangement : Nano-Domain \rightarrow

{	Microdomain \rightarrow Domain
	Optical Texture
	Microfibril \rightarrow Fibrils
- Variety of Cluster Single, Double, Triple, Layers
 Size - Nano to Several meters
 Nano-Carbons and their Units
- Graphene \rightarrow Hexagonal Sheet (Size and Shape)

Inter-unit Spaces: Voids, Defects, and Vacancy

Figure 3. Structural hierarchy of carbon materials.

Since carbon is basically porous, the surface within its pores is the origin of its functional performances. Thus, the pore and pore wall must be described at the same time to understand the carbon structure. The wall structure can be described as explained above. The graphitic extent of the pore wall must be considered because is very important for activated carbon, too.

Pore size, depth and volume have been described as the important factors for activated carbon.⁸ Edges of hexagonal planes and their stacking unit should be described in terms of either basal plane or prismatic edge. Substitutional groups on the edge and heteroatoms in the first array of the hexagon plane should be also taken into account.⁹⁻¹¹ Figures 5-7 show some special characters of activated carbon.

Such carbon structure is produced through a series of carbonization, graphitization, gasification and successive modification,^{12,13} as shown in Figure 8.¹³ The first two

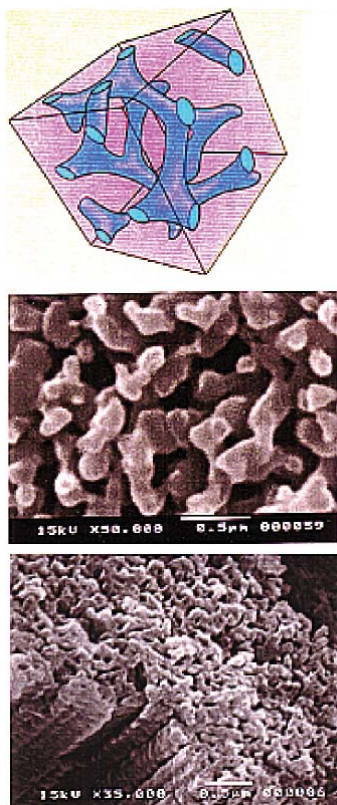


Figure 4. Voids among structural units in the mesophase pitch and pitch fiber.

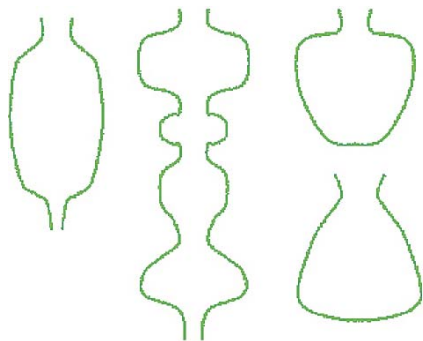


Figure 5. Schematic shapes of pores in activated carbon.

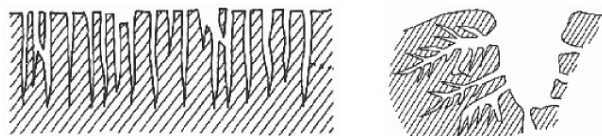


Figure 6. Schematic pore images of activated carbon fiber and activated carbon.

processes are included in the transformation of organic substrates to the graphitic materials through the carbonaceous intermediates. The last two are the post-treatment of carbon into the active surface materials. It must be mentioned that the interface properties are particularly important in the composite material.

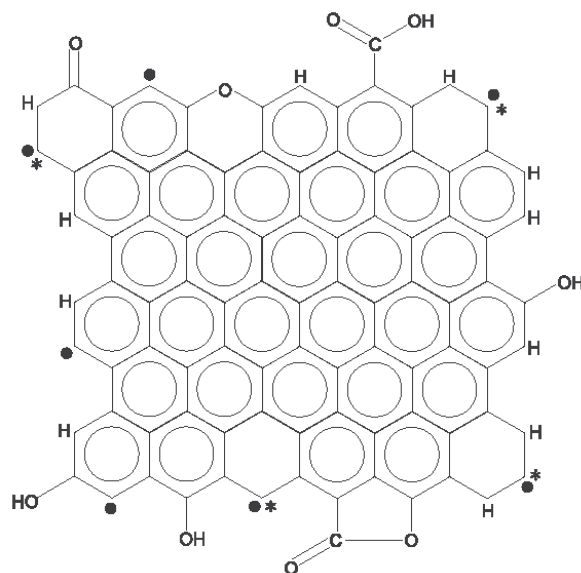


Figure 7. Surface oxygen functional groups of activated carbon fiber. The structure is representative of an activated carbon with a crystalline width of 1.5 nm and an elemental analysis of 87.5% C, 11.3% O, 1.2% H. • represents an unpaired σ electron; •* represents an “in-plane σ pair” with * being a localized π electron.

Such transformation includes reaction chemistry and phase change from the organic precursors to solid carbon, defining the structure of carbon, and hence their properties. Such series of chemical and physical transformations must be governed by the properties of organic substrates, solvent materials and the catalyst. Polycondensation and polymerization into less-volatile and non-fusible carbonaceous products define the phase of the carbonization to govern the extent of alignment of aromatic sheets which decides the alignment of carbonaceous hexagonal planes at every stage of structural hierarchy. Carbon precursors of carbonaceous intermediates can be aromatic liquid crystals, whose properties are governed by the molecular and compositional chemistry. Catalyst is a very important tool to control the molecular and compositional chemistry at the transformation process of organic substrates into carbon, throughout carbonaceous intermediates.

2. Catalytic Carbonization

Catalyst governs and controls the reaction phase as well as the chemistry involved in carbonization. The roles of catalyst in chemical and physical transformation must be grasped in every step of the catalytic carbonization. The catalyst remaining in the product is sometimes fatal, so it must be completely removed, or

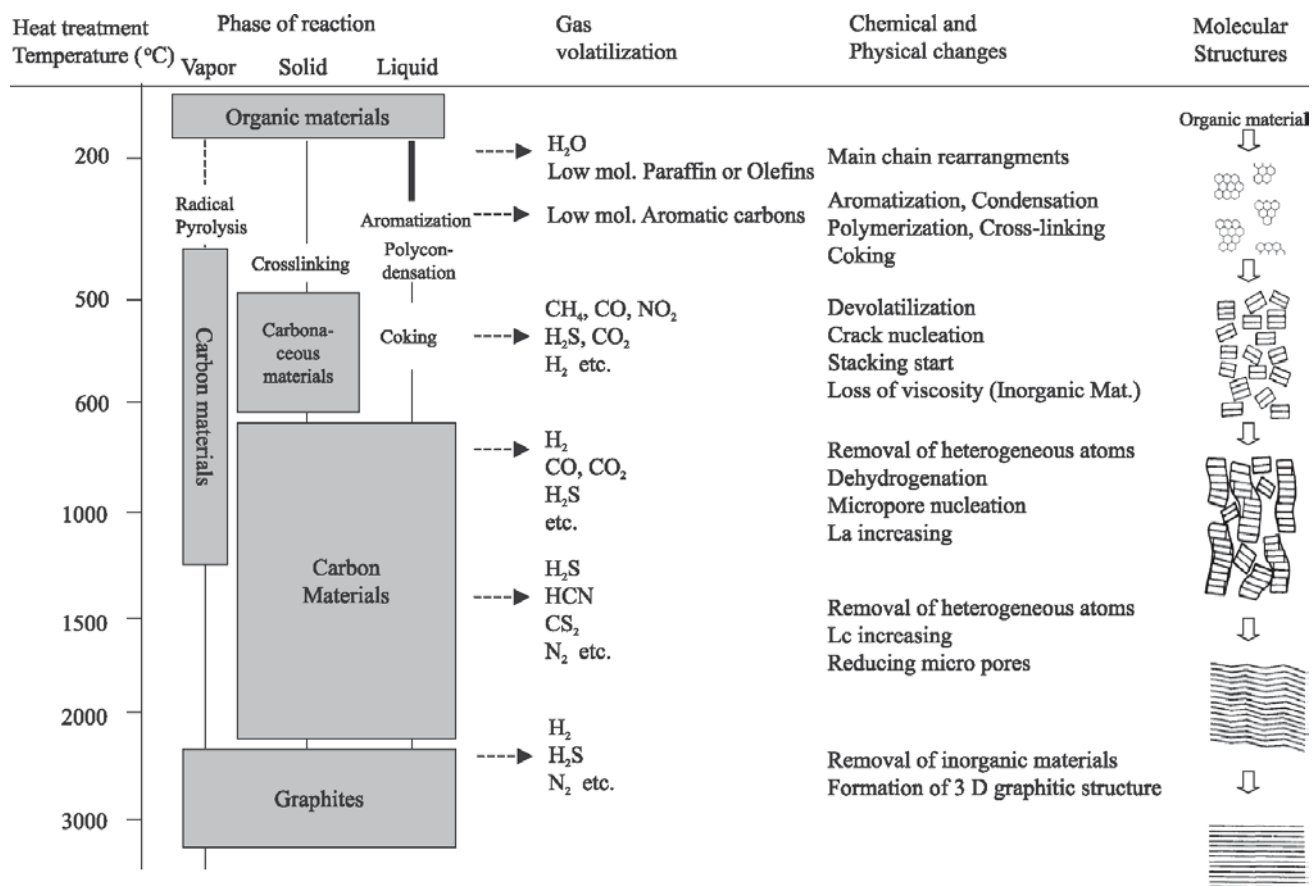


Figure 8. Carbonization and graphitization of organic materials.

favorable as a component of the composite. The removal tends to be very tedious, but it can introduce extra-properties to the product such as controlled porosity. We can choose the thermal carbonization without any catalysts.

Catalysts in the carbonization can be acidic, basic, hydrogenative or dehydrogenative (hydrogen transfer), oxidative and oxygenative to catalyze the condensation/cracking, hydrogenation/dehydrogenation, oxidation/oxygenation reactions of the precursors and intermediates to influence yield, rate and phase of the carbonization, defining the final carbon structure.

Long residence time of the precursor and intermediate leads to the carbon formation on the solid catalysts, major poisoning on the industrial catalyst.

A series of Lewis acids such as AlCl₃ and FeCl₃ have been examined in the carbonization,¹⁴⁻¹⁶ whose condensation activity increased markedly the carbon yield. AlCl₃ has been recognized an excellent catalyst to provide anisotropic carbon from aromatic hydrocarbons, except for benzene, at a very high yield. It removes alkyl groups and sulfur through the cracking reactions. In contrast, the dehydrogenation activity, mainly with Lewis acids of

transition metal salts and alkali bases leads to a rapid solidification, prohibiting the development of the liquid crystal stage to result in the isotropic, less graphitic carbons. Such catalysts are very difficult to be recycled. Their remaining prevents the production of pure carbon, so, their influences on the graphitization must be taken into consideration.

3. Catalytic Synthesis of Feed and Intermediate for Carbon

Feeds for commercial carbons are produced in the petroleum refining and coal tar industries. Petroleum refining processes using catalyst such as FCC, hydrocracking, hydrodesulfurization, and hydrogenation provide bulk feeds for the carbon. The catalyst is quite influential on the structure and hence the properties of feeds. Aromaticity, naphthenic structure and heteroatoms are three important factors to define the quality of feeds. Coal tar and coal liquefaction derived liquids are also important feeds for bulk carbon. Hydrogenation and hydrogen transferring treatment can be applied to up-grade their

properties as carbon feeds. It must be noted that such processes are designed for the refining activity and not to produce the carbon feeds. The main refining products control the cost. Otherwise the cost should be very high. Such feeds are often heat-treated, gas-blown or vacuum-distilled to cut the lighter fraction. Carbon yield and softening points are controlled by such treatments.

3.1. Mesophase pitch

Mesophase pitch (namely anisotropic pitch) has been recognized as a precursor for the high modulus carbon fiber through the spinning, stabilization, carbonization and graphitization steps.¹⁷⁻¹⁹ Isotropic pitch can be used as a precursor for the general proposes carbon fiber through similar steps. The major difference between the two precursors is the molecular ordering of aromatic stackings, which survives in the fiber preparation steps, govern the graphitic structure along the fiber axis. The mesophase pitch can satisfy both molecular ordering and spinnability at adequate melting viscosity by the structure and distribution of the components. Naphthenic and alkyl groups seem to be essential among the aromatic molecules. The molecular species forming the mesophase pitch are called mesogen while the disturbing species against the disk-like liquid crystal natures are non-mesogen. Several procedures are proposed to prepare the mesophase pitch where thermal preparation of the mesogen molecules from species, in the pitch, and concentration of the mesogen, by removal of non-mesogen, are thermally performed, as well.²⁰⁻²³ The concentration can also be performed under vacuum by rapid gas flow. All thermal processes suffer from a low yield and they produce the least variety of the mesophase pitches since the thermal process synthesizes

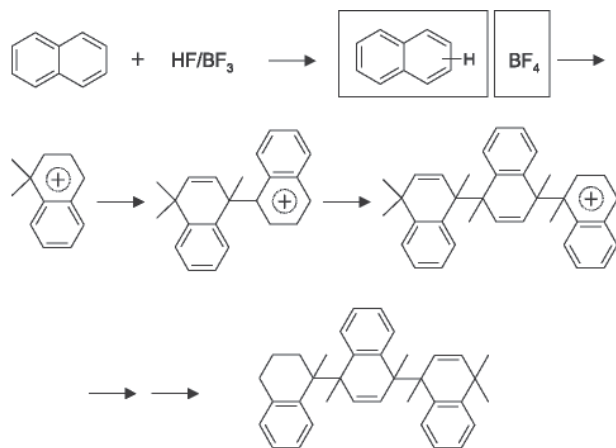


Figure 9. Catalytic synthesis of mesophase pitch from aromatic species using HF/BF₃ catalyst.

very limited species into the mesogens, of restricted structure, according to their thermal reactivities.

The authors and Mitsubishi Gas Chemical Co. developed a catalytic process of mesophase pitch syntheses from aromatic species such as pure naphthalene, methyl-naphthalene or their mixtures, using HF/BF₃, a strong Friedel-Craft catalyst for aromatic condensation.²⁴⁻²⁶ HF/BF₃ is a unique acidic catalyst which allows its complete removal from the product, and its recovery and repeated use because of the low boiling points of the both components.

Figures 9 and 10 describe the reaction scheme of aromatic condensation and production flow, respectively.^{25,26} The present process demands a single step to complete the conversion of aromatic species into mesogen molecules, hence no separation of non-mesogen is basically necessary. Naphthenic structure is induced by the condensation without spontaneous dehydrogenation. An incomplete conversion of aromatic species may require the thermal separation of non-mesogen species while the thermal process enhances further condensation and dehydrogenation. Hence, the properties of two mesophase pitches are very different even if the same starting aromatic species and catalyst are applied. This is the most successful catalytic process in the preparation of mesophase pitch.

Table 1. Properties of synthetic mesophase pitches

	S.P./ °C	H/C	f _a	Lc (002, nm)
Naphthalene pitch (8v26m)	237	0.65	0.95	3.0
Methylnaphthalene pitch (ST14)	205	0.69	0.86	4.1
Methylnaphthalene pitch (ST15)	227	0.67	0.90	4.0
2,6-dimethylnaphthalene pitch (EP415)	237	0.72	0.84	10.4

S.P.: softening point measured by flow test method; f_a: aromaticity.

Table 1 summarizes the properties of some AR mesophase pitches. The molecular structure of their mesogen molecules are illustrated in Figure 11.²⁵

The very important feature of the process is to allow molecular diversities of mesophase pitch by selecting the starting species, of which structural characteristics survive in the product pitches, controlling their structure and hence properties. One of the most marked features is that the planar stacking of mesogen molecules is strongly influenced by the alkyl substituent on the aromatic plane.²⁵ The stacking is also function of the temperature although it is thermally reversible or restored by annealing.²⁶⁻²⁹ The stacking of the mesogen appears to inherit the stacking and orientation of hexagonal planes and to lead to the high graphitizability after the graphitization in the carbon.

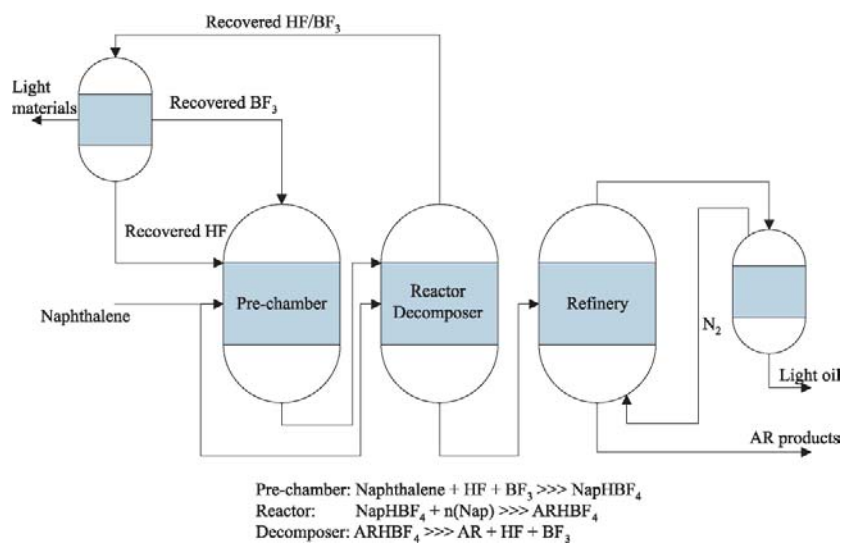


Figure 10. Schematic flow chart of MGC AR process.

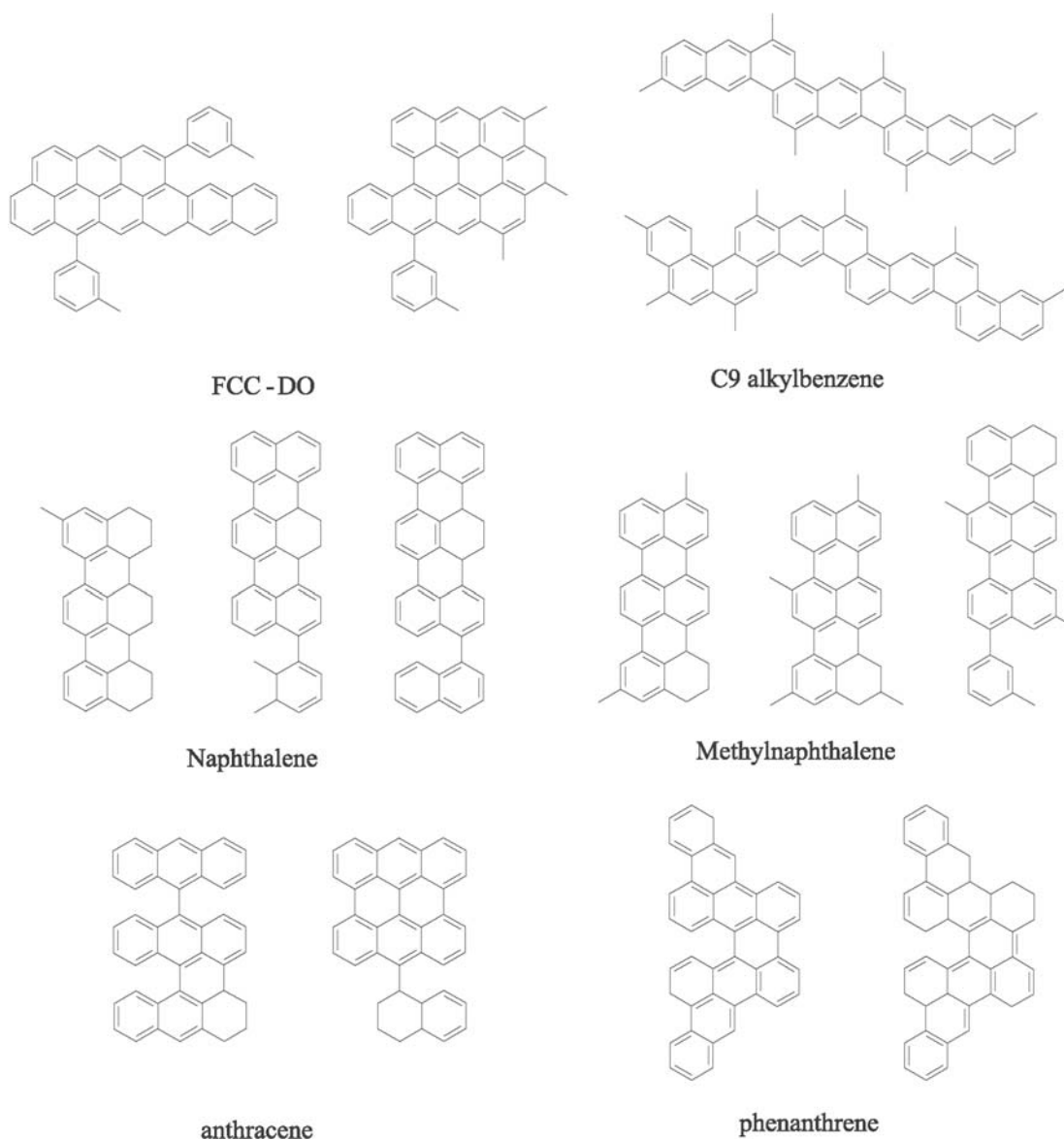


Figure 11. Typical mesogen units in various mesophase pitches.

Catalytic process can modify the pitch by further hydrogenation, hydrogen transfer, alkylation, trans-alkylation, addition and coupling although no commercial application is established. Thermal oxidation by air-blown is also successfully applied.

3.2. Catalytic polymerization into glassy carbon

Glassy carbon has been appreciated in industrial applications as a less permeable carbon in spite of its many closed pores. The glassy carbon is derived through the solid phase carbonization where aromatic components and their clusters are rather fixed in their special location, in the starting substances or products, producing the smallest possible mobility during their transformation into carbon in the solid state, allowing the least ordering in the stacking and alignment of the product carbon. Thermosetting polymers or pitch-like materials stabilized or solidified at the early stage of the carbonization can give glassy carbon by preventing the growth of aromatic or hexagonal stacking and their alignment.

A large number of catalysts are applied to assist the formation of three dimensional networks at the polymerization. Phenolic and furfural resins are the typical precursors of the thermosetting polymers for the glassy carbon.

Thermoplastic polymers, such as polyacrylonitrile or pitches, are stabilized through the air oxidation to be non-fusible by the three dimensional network through the covalent and/or Van Der Waals bondings around oxygen

functional groups.³⁰ Dehydrogenation of the large plane into high aromaticity, tends to raise the softening point of the carbonizing substances to keep the solid phase while the condensation progresses to raise further the softening point during the carbonization and successive calcination.

It must be noted that the aromatization and/or carbonization to form carbon hexagon proceeds in the solid phase to give usually isotropic and less graphitic carbons. Figure 12 illustrates the paths from AR into the soft and hard carbons by modifying the carbonization stages through the selected treatment.

3.3. Catalytic pretreatment of precursors

Carbon precursors of industrial feeds often carry contaminants which may inhibit the desired carbonization (growth of optical anisotropy, for example) or stay in the product carbon as unwanted impurity. The impurity reduces the strength and electric conductivity and increases the reactivity for unwanted gasification.

Hydrogenation and cracking can modify the carbonization properties since the partial hydrogenation and removal of long alkyl chains are recognized as very favorable for anisotropic development through the controlled carbonization reactivity and co-carbonization activity by dissolution and hydrogen transfer.

Such reactions are performed in the presence of the catalysts. HDS, HDN and HDM are performed over NiMoS and CoMoS catalysts which are supported on alumina base oxides.³¹⁻³³ Current acidity of the support

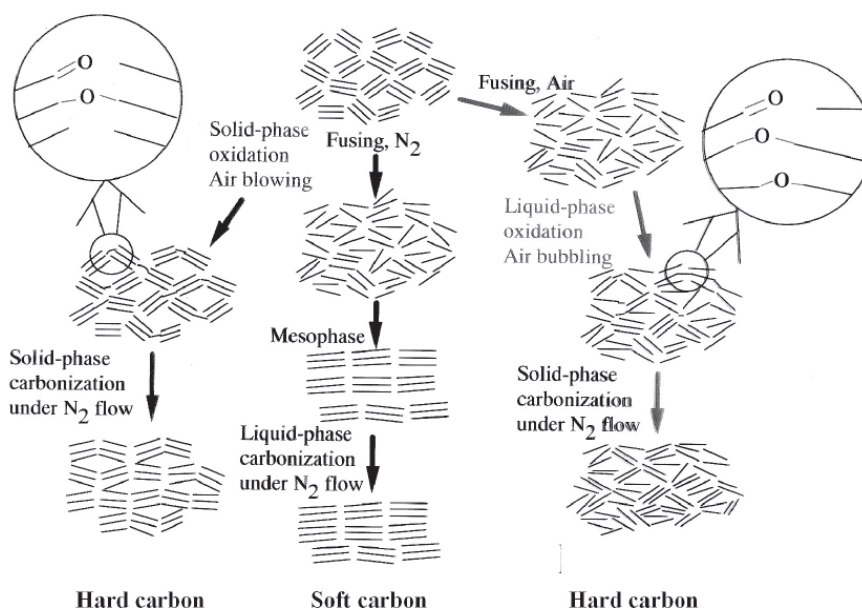
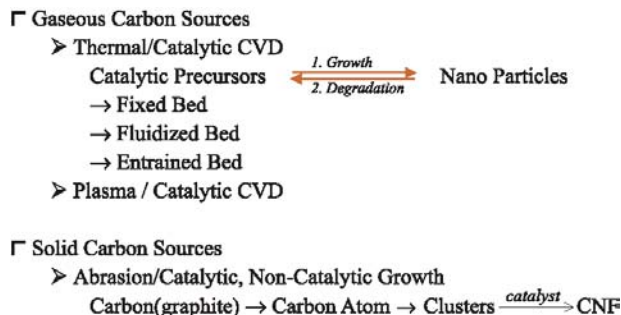


Figure 12. Soft and hard carbons from AR pitch by modifying the carbonization stages.



should be highly considered. Zeolite can be acidic dealkylcarbon cracking and partial aromatization catalyst.

4. Catalytic Carbon Growth

Currently, carbon nano fibers attract broad interest of researchers and engineers to develop nano carbon materials for much higher performance or new application of carbon. Carbon nano fibers are believed to grow over the metal catalyst particles. The carbon source for CNF

Figure 13. Carbon sources for CNF.

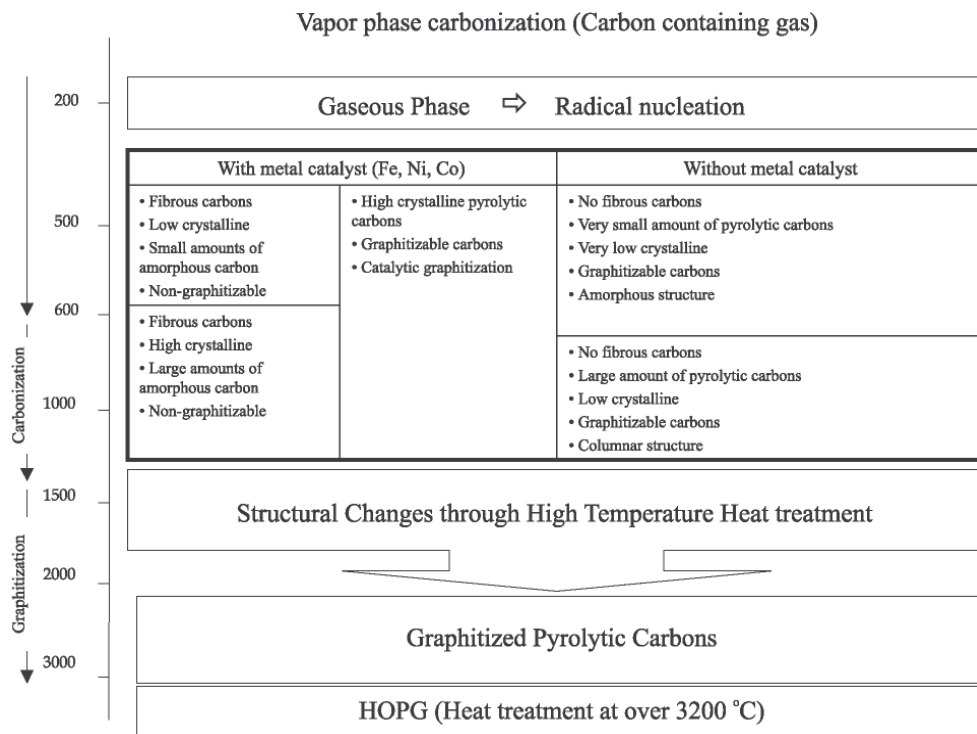


Figure 14. Vapor phase carbonization. (HOPG: highly orientation pyrolytic graphite).

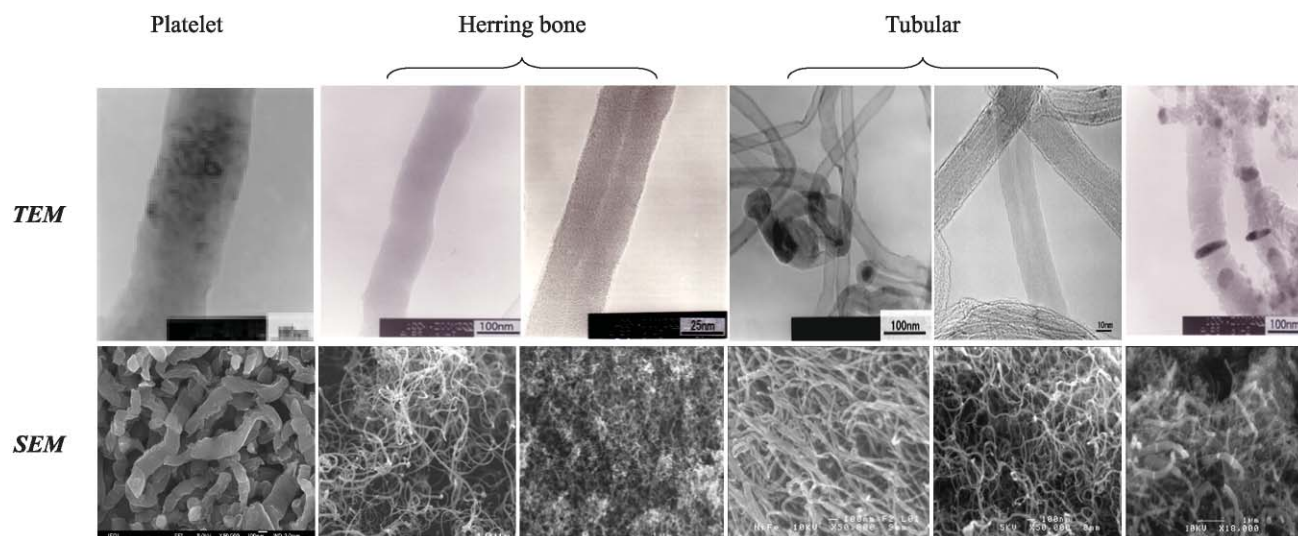


Figure 15. Representative carbon nano fibers.

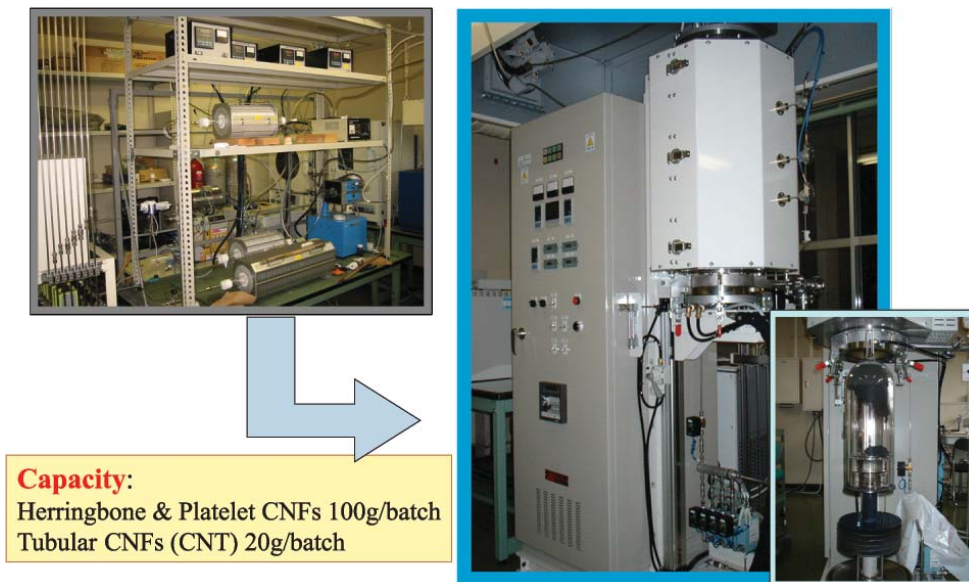


Figure 16. Fixed bed reactor for CNF growth.

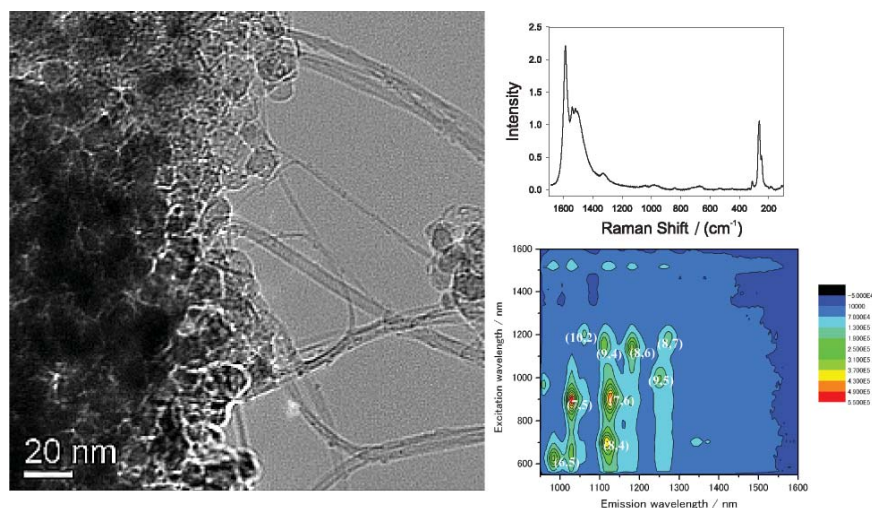


Figure 17. Preparation of single nano tube.

can be gaseous hydrocarbons and solid carbon as summarized in Figure 13. Solid carbon can be abraded by laser or arc discharge into carbon atom or its cluster in the gas phase. The hydrocarbons and CO react with the metal particle to produce carbon on the surface. Hydrogen is often applied as carrier gas which is expected to control the thermal reactions.

Figure 14 summarizes vapor phase carbonization, emphasizing the importance of the catalyst to define shape, size and property of the resultant carbon. Figure 15 illustrates the representative carbon nano fibers, and emphasizes the continuous change of hexagonal alignment along the fiber axis in the CNF.¹³ Such changes are controlled by the catalyst, reaction temperature, and

hydrocarbon feeds.³⁴⁻³⁷ The authors emphasized that nano catalyst particles are prepared through the degradation of as-prepared metal catalyst during the reduction of oxide precursor and reactivity with hydrocarbons.

Figure 16 illustrates the fixed bed reactor for CNF growth. A small scale boat and fairly large scale filter are applied for containing the powder catalyst. The filter type catalyst container allows free growth of the CNF over the metal particle. Smaller catalyst particles carried on the adequate support tend to produce thinner fibers.^{38,39} Single wall carbon nano tube and other thin nano fiber are illustrated in Figures 17 and 18.

Figure 19 illustrates the growth mechanism of CNF over the metal particle. It is noted that the catalyst shape

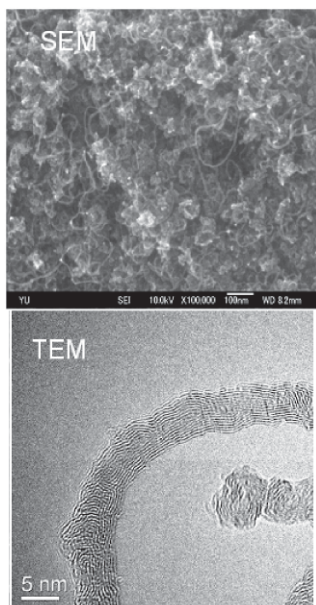


Figure 18. Preparation of thin nano fiber.

and size define those of the fiber and that the shape and size of the catalyst are subjected to the reaction conditions as well as the catalyst preparation procedure.

Figure 20 illustrates the morphological change of the catalyst particles during the pretreatment and CNF growth.³⁶ It is very true that the nano particles are produced through the catalyst degradation. Nevertheless, it is not clarified

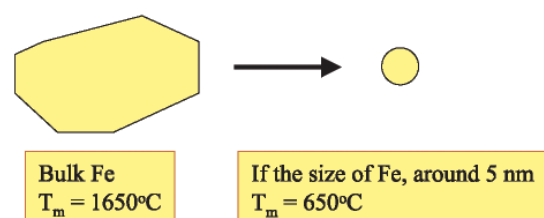
yet which mechanism and factors of the starting metal work for defining the size and shape of the degraded particle.

When the catalyst, supported in the carbon or other substrates, grows the CNF on the substrates,⁴⁰ CNF-substrates are prepared as new composite materials.

5. Catalytic Activation of Carbons

Activated carbon has been an indispensable material for many years due to their surface functions.

H₂O/CO₂ gasification has been the most important process to introduce pores in the bulk carbon through the selective gasification of particular groups of carbon on the surface. The graphitic carbon has been believed to be difficult to be activated by such conventional procedure. In addition, local shrinkage of the graphitizable carbon at the activation stage tends to remove the pore. Gasifying catalysts and oxidants are important to introduce pores regardless of the type of carbon material involved. Another procedure is to use nano template (nano size or nano space) to introduce pores, removing fine particles in the carbon body.⁴¹⁻⁴⁴ Pores are formed along the path of template removal or in the pore wall of the template. Template can work as the catalyst of gasification and carbonization to control the pores and carbon produced over their surface. The cracks formed in the carbon at the



If the size of Fe is around 5 nm		
Over 700°C	Not Crystalline	Round
650 – 700°C	Pseudo-crystalline	Round, Ellipsoidal or Crystal Shape
Under 650°C	Crystalline	Crystal Shape

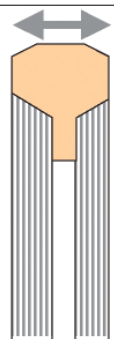
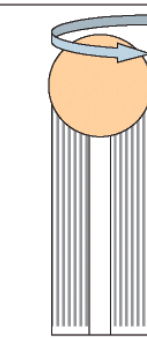
Preparation of carbon nanofibers using Fe catalyst and CO/H ₂ gas mixture	
650-700	Over 700
High Crystalline CNF	Low Crystalline CNF
Only Vibration	Vibration & Rotation
	
No helical structure of graphene sheet stacking	Helical structure of graphene sheet stacking

Figure 19. Growth models of CNF over the metal particle.

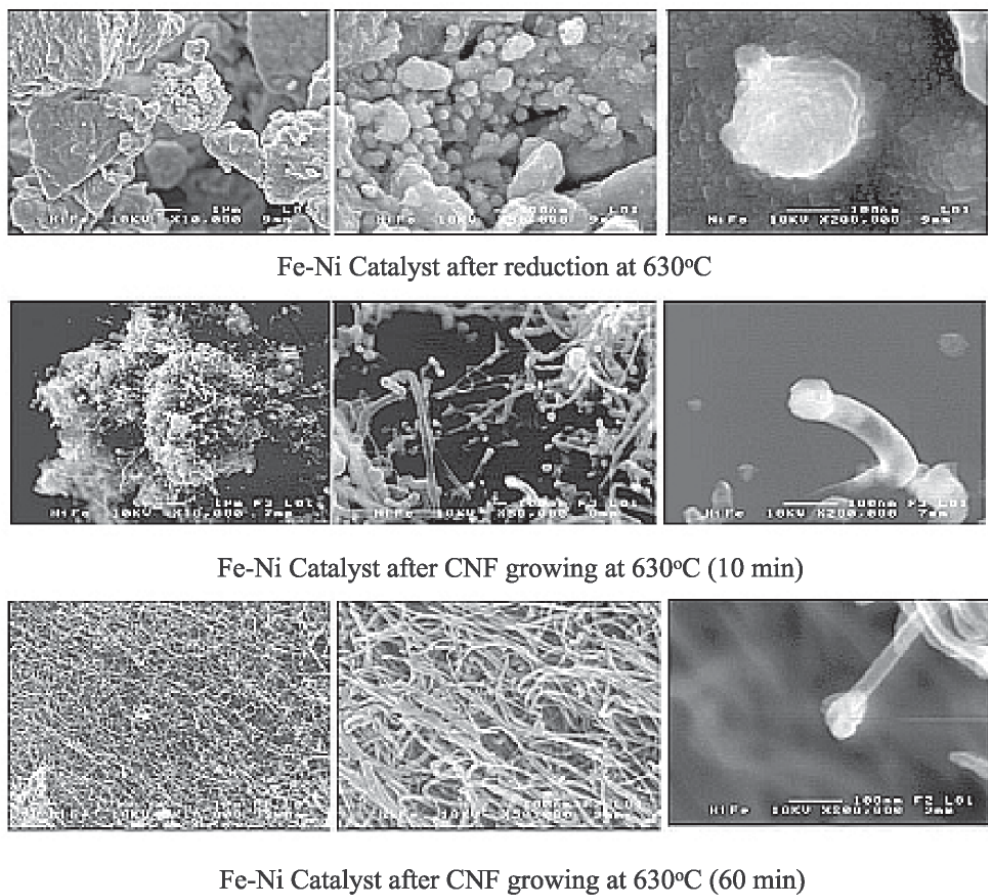


Figure 20. Change of the catalyst particles during the pretreatment and CNF growth.

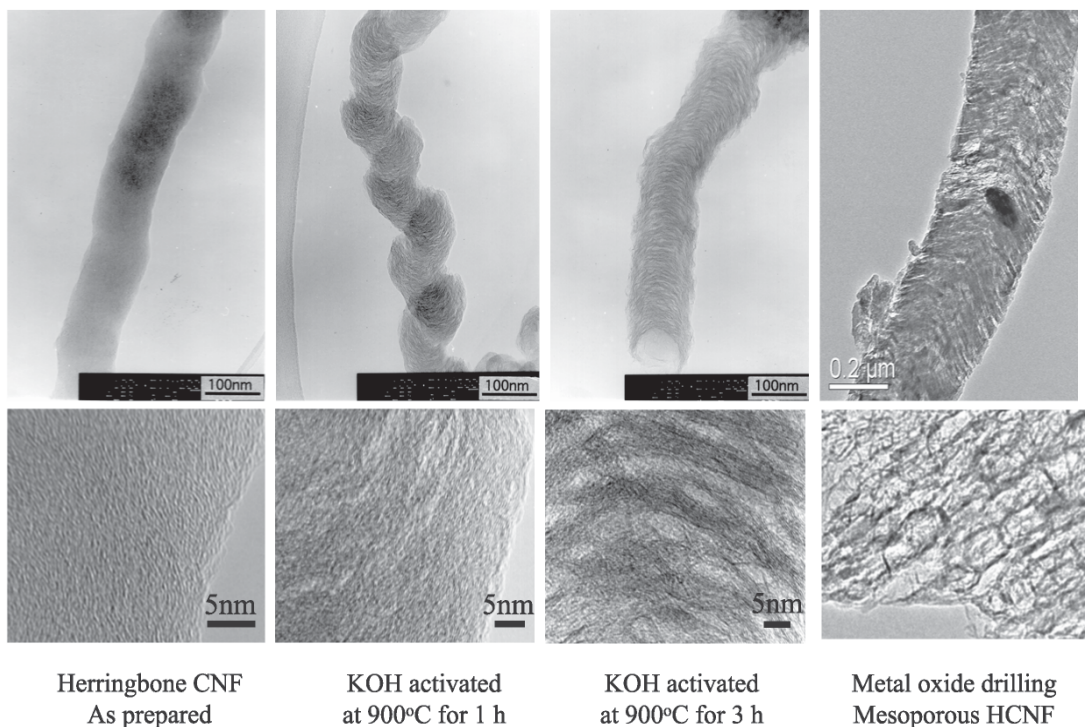


Figure 21. Typical examples of herringbone type CNF (HCNF) activated with KOH and metal oxide.

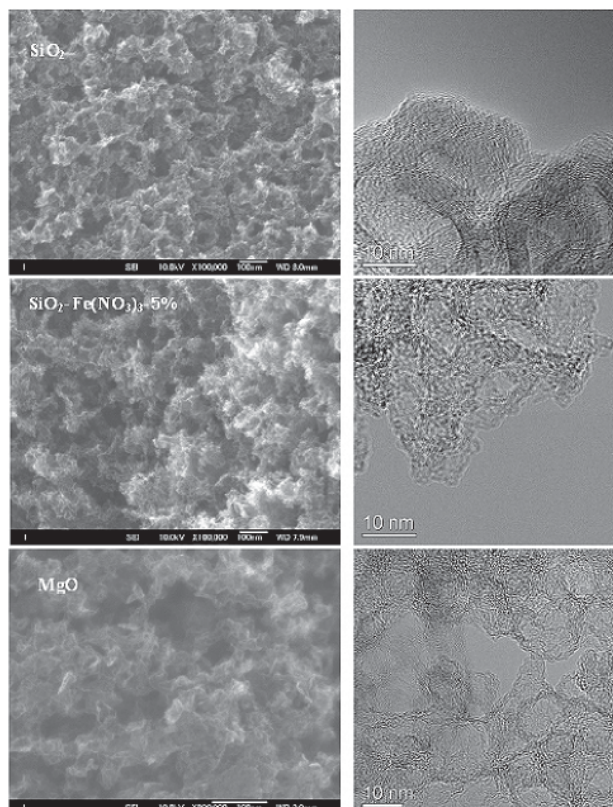


Figure 22. SEM and TEM image of mesoporous carbon prepared from mesophase pitch and nanosized particles (scale bar of SEM photograph: 100 nm).

calcination stage are also influenced by the template.

The gasification can take place over a single structural unit or among the units. Intra-pore must be micro in the single unit while the inter-pore can be the mesopore formed among the nano particles.

Currently, KOH activation is reevaluated to provide the largest surface area to any carbons, and to activate the graphitic carbons after the calcinations.⁴⁵⁻⁴⁷ It is a powerful agent, whereas its severe corrosion and production of H₂, as well as metallic potassium, may be considered to be difficult to build in large scale production.

Figure 21 illustrates typical examples of herringbone type CNF activated with KOH⁴⁷ and metal oxide.⁴⁸ KOH provided micropores among the CNF structure while the oxide drills mesopore along with nano rods of herringbone structure. KOH must be reduced to metallic potassium to invade between the hexagon planes, and to produce micropores.

Nano particles are templates for the nano pores when nano particles are removed by extraction,⁴⁴ and vaporization. SiO₂ has been broadly studied but its extractive removal requires HF or strong alkali. Its vaporization takes place above 2000 °C after the formation of carbide. In contrast, MgO and CaO are more easily removed by acidic extraction.⁴⁹

Another possible template is a transition metal oxide which can be removed by extraction and vaporization from the carbon. Its reduction by carbon wall gasifies the carbon to modify the pore during the carbonization. As shown by SEM and TEM, the mesopores produced by fine particle templates are illustrated in Figure 22.

Mesopores are introduced among the nano carbon particle which can be derived through sol-gel procedure.^{50,51} The catalyst used for the condensation of monomers into the thermosetting polymer may stay among the nano carbon particles to gasify the carbon particles at their intraparticle as well as interparticle positions to form additional micropore to modify the mesopore. Catalytic roles are carefully taken into account in this procedure.

The activated carbon can be active because of surface functional groups as well as its large surface area, and selected pore size and distribution. A single activation procedure cannot always optimize both. Post-oxygenation to increase oxygen functional groups over the wall of pore, after the primary activation, increases the surface area. The catalysts as well as strong oxidants are useful for such purposes.

The key is to perform such oxygenation at lower temperature than that to decompose the groups. It must be

1a	2a											3a	4a	5a	6a										
3 Li	4 Be											5 B	6 C	7 N	8 O										
11 Na	12 Mg	11b	12b	13b	14b	15b	16b	17b	18b	19b	20b	21b	22b	23b	24b	25b	26b	27b	28b	29b	30b	31b	32b	33b	34b
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se										
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te										
55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po										

Figure 23. Several elements (Bold letter) with catalytic activity for the graphitization.

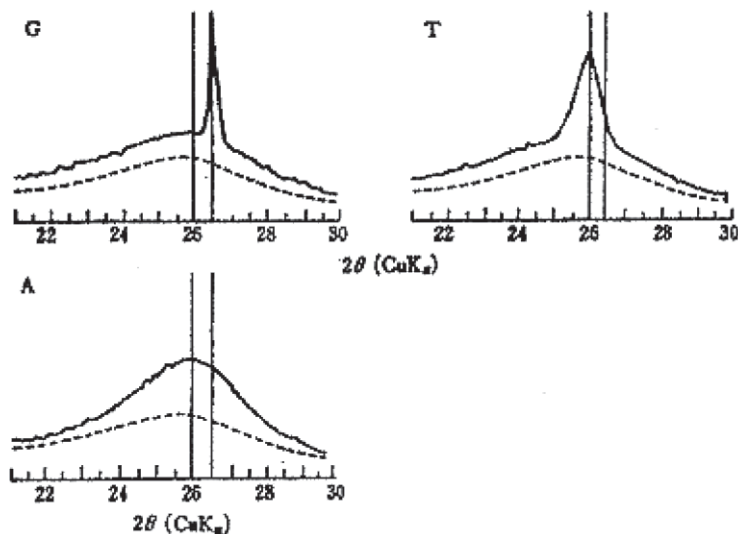


Figure 24. Three mechanisms for the catalytic graphitization. G: Catalytic graphitization; T: T effect; A: A effect.

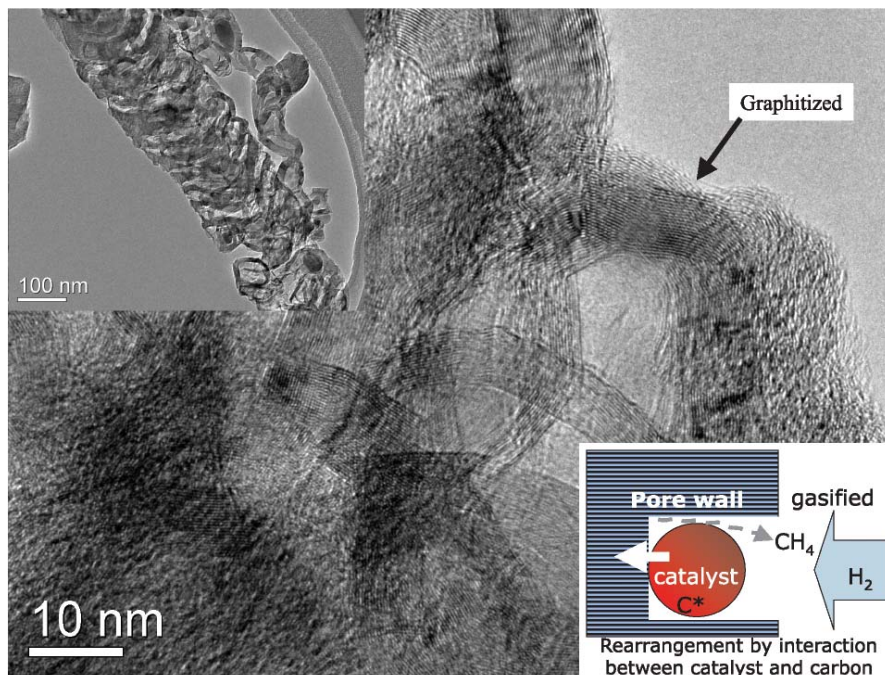


Figure 25. Catalytic graphitization of a herringbone CNF treated with 5% Fe at 850 °C under H₂. Gasification and C formation (rearrangement) > Catalytic graphitization, depending on catalysts and conditions.

noted that the thermal elimination of groups at a particular temperature can induce an active vacant site over the edge of the hexagonal plane, dangling or producing benzene-type bonds at the periphery of the hexagons.

6. Catalytic Graphitization

Highly graphitic materials are always wanted to be prepared at lower temperatures. The catalytic graphitization has been explored in many instances.⁵²⁻⁶⁰ The graphitization stage of arc carbon electrode, prepared from the needle

coke must suppress the puffing caused by sulfur evolution, at this stage. For this purpose, iron oxide is dispersed with the binder pitch into the coke. The iron oxide is believed to accelerate the graphitization at the same time. There are several mechanisms proposed for such additive to suppress the puffing. The catalytic graphitization is one of the mechanisms.

Many elements in the periodical table were reported to show catalytic activity for the graphitization of carbon materials,⁵⁹ as summarized in Figure 23, although the effects are not always defined or pointed out.

The authors emphasized activities of Cr_2O_3 and MnO_2 around 1300-1400 °C. MoO_3 and V_2O_5 showed their activity at much higher temperature beyond 2000 °C^{52,53}. Oya⁵⁹ classified the graphitization activities into three categories, which give very sharp peak at 26.5° (graphitization), rather than a broad peak around 26.5° and fairly sharp peak at 26.0°, in the XRD of the carbon samples graphitized with the respective catalysts. In all cases, some graphitic or ordered stacking structures are certainly enhanced or introduced, however industrial applications have never tried, except for Fe_2O_3 , any other puffing inhibitor on the petroleum coke. Only B_2O_3 has been applied for the graphitization to produce the lithium battery anode. MnO_2 and Cr_2O_3 may be applicable because of their activity at lower temperature. Three mechanisms for the catalytic graphitization have been proposed as summarized in Figure 24.⁵⁹

Figure 25 shows a herringbone CNF treated with 5% Fe at 850 °C under H_2 . The gasification to yield CH_4 provides mesopores as described above. The wall remaining after the gasification is highly graphitized in the whole fiber as shown by the defined stacking under TEM.

7. Conclusions

Catalysts in synthesis of carbon and carbon precursors are certainly useful to prepare carbons of higher performances at lower cost. The catalyst can control the reactions in terms of reaction chemistry and phases involved in all stages of carbon preparation.

The separation of the catalyst must be carefully designed in every step. In particular cases, remaining catalysts are convenient as components of the novel composite. However, the remaining catalysts are often unwanted and should be removed and recycled if possible. It is not easy to recover the solid catalyst from the carbon without significant degradation of the carbon and chemical changes of the catalyst material. Thus the catalyst removal must be designed not to hurt the carbon properties and shape. In this sense, the synthesis control and modification of the carbon precursors are most useful. Catalytic activation can be another use of catalysts in carbon industry since they can be useful to enhance the surface activity of activated carbon.



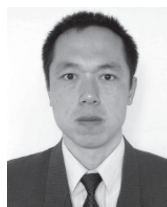
Isao Mochida (Kyushu University – Japan): Professor Emeritus at Kyushu University, Isao Mochida was awarded his Ph.D at Tokyo University in 1968. Working on carbon science, petroleum and coal processing, and catalysis, Prof. Mochida has published over 800

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