

2. Literature Highlights and Methodology

The oxidative dehydrogenation (ODH) of alkyl-aromatics was reported in the early 1960s. The process proceeds in the presence of oxygen according to the equation below.



This process was suggested to overcome the drawbacks of the normal dehydrogenation process. This reaction is exothermic and proceeds at lower temperatures (as low as 380 °C). In addition, the removal of hydrogen by reaction with oxygen shifts the equilibrium to the products side achieving a complete reaction.

Many catalysts were suggested for the ODH of alkyl-aromatics. First catalytic systems studied for this process were those based on the promoted inorganic oxide catalysts.

SnO₂-P₂O₅ system was found to have activity of about 30 % conversion with 80 % selectivity to styrene at about 550 °C¹. ZrO₂-P₂O₅ system was found to be more active at the same temperature. A conversion of about 55% with 80 % selectivity to styrene was observed². Cerium pyrophosphate system was found to exhibit 76% conversion with up to 90% selectivity at 605 K³.

It was reported that each of the studied systems exhibits an induction period. The enhancement of the catalytic systems during this induction period is characterized by the building of a uniform thin layer of carbonaceous products (coke) on the surface⁴.

Deposition of coke on the catalyst is one of the main problems encountered in the high temperature processes for catalytic conversion of hydrocarbons. This coke is normally a major cause of the catalyst deactivation. However, it can in some cases promote the activity as a result of its own catalytic activity. It was found that the ODH of alkyl-aromatics is among these processes promoted by coke deposition^{5,6}.

2.1 The element carbon and its importance in catalysis

Carbon which was discovered in the prehistory is an abundant nonmetallic tetravalent element. There are 15 known isotopes of carbon among which two are stable, naturally-occurring [carbon-12, or ^{12}C , (98.89%) and carbon-13, or ^{13}C , (1.11%)] and one is unstable, naturally-occurring, radioisotope [carbon-14 or ^{14}C].

Being able to bond with itself and a wide variety of other elements, carbon forms nearly ten million known compounds. In addition, it can take different molecular configurations (allotropes) to form a wide range of substances with distinguishable characteristics.

The three mostly known allotropes are graphite, diamond and amorphous carbon. Other allotropes include fullerenes, chaoite, lonsdaleite, carbon nanofoam, carbon nanotubes, aggregated diamond, lampblack, and 'glassy carbon'.

Carbon materials have been widely used as supports of several catalytic systems because they can exhibit very wide variety of porous structures and they can be considered as inert materials⁷. The use of carbon materials as catalysts, however, was lately addressed because of the lack of fundamental understanding in the past of many aspects of the physical and chemical characteristics of carbon materials⁸.

Carbon was reported to catalyze several reactions including hydrogenation, oxidation, reduction, polymerization and chlorination^{7,9}.

A correlation between the catalytic properties and carbon's electronic properties is claimed by Coughlin⁹. The author concludes that "many of the catalytic and adsorptive properties of carbon can be understood in terms of structure, electronic behavior and surface chemistry".

A good correlation between carbon surface area and its performance as a support was reported. Nonetheless, such correlation was not reported for its behavior as a catalyst. However, its surface chemistry plays the major rule⁸. Hence, the

development of carbon catalysts depends on the better understanding of the chemistry of the carbon surface and not only on the surface area and porosity.

2.2 Carbon materials in the oxidative dehydrogenation process

As mentioned above, the studies of the oxidative dehydrogenation of ethylbenzene over promoted metal oxide systems have given an indication of a significant role of the deposited carbonaceous materials in promoting the catalytic activity.

These observations lead to the study of the catalytic activity of the oxidation condensation products (OCP) in the aim to develop new profitable industrial processes. Main areas addressed in the study of the catalytic activity of OCP were the deposition and burning of OCP¹⁰, the role of ethylbenzene, styrene and oxygen in this process^{6,10} in addition to the role of temperature and the nature of the catalyst.

One of the first observations was reported by Alkhazov et al.¹¹. They studied the role of condensation products in the ODH on aluminum oxide catalyst. They found that styrene and carbon oxides form at increasing amounts until a monolayer of condensation products is formed on the surface (they used the term monolayer to refer to the minimum amount of OCP necessary to cover the catalyst surface). This was not an enough proof of the action of coke as the active phase, but the separated condensation products were tested and found to be active.

The same was also observed by Tagiyev et al.⁵ on CaO/SiO₂ system, Schraut et al.¹² on zirconium phosphate, Dziewiecki et al.¹³ on nickel phosphate and Vrieland³ on Metal pyrophosphates. Cadus and co-workers¹⁴ who studied the action and nature of active coke over alumina suggested a redox-type mechanism. In their attempts to explore the nature of the active coke¹⁵ they used burn-off experiments, temperature programmed oxidation, ammonia desorption, XPS, electron paramagnetic resonance (EPR) and secondary ion mass spectrometry (SIMS). They stated that none of the used techniques individually offers precise information, but considering the obtained results altogether, they reported about oxygen-containing functional groups in the active coke with evidence that only the quinone/hydroquinone and aroxyl/phenol

pairs can play a role in the suggested redox mechanism. Additionally, they stated that the active coke is composed of a system of condensed aromatic rings.

Main observations of the mentioned studies of the carbon deposits in ODH reactions were:-

1. Coke and not the metal oxide is the catalytically active phase.
2. The reaction proceeds via an oxidative dehydrogenation mechanism rather than normal dehydrogenation.
3. Surface oxygenated groups plays the major role in determining the catalytic behavior of the active coke.

After the many evidences that the carbon deposits are the real catalysts in the ODH process over inorganic oxides, the use of carbon materials as catalysts for the oxidative dehydrogenation of alkyl-benzenes has attracted a great interest.

Among the carbon materials tested as catalysts for ODH of ethylbenzene one finds active carbons^{6,16-22}, charcoal catalyst²³, carbon nanotubes^{22,24-26}, activated carbon fibers^{27,28}, graphites¹⁶ and onion-like carbon materials²⁹.

In the study of active carbons' catalytic activity, different types of oxidative treatments of the material were tested. Gas phase treatment was found to be more effective than liquid phase treatment²¹, it improved the performance and was associated with the increase in the amount of carbonyl/quinone groups. By selective removal of surface functional groups (in the same paper), carbonyl/quinone were found to be the most active surface groups with a linear relationship between catalytic activity and the amount of these groups on the surface. By performing kinetic modeling experiments, the main reaction was found to occur by a redox mechanism, which is the rate determining step¹⁸. Catalyst deactivation²⁰ was the main disadvantage of the process which is a result of the formation of oxygenated coke which blocks micro pores and increases reactivity towards oxidation. In the study of the Influence of the textural properties²², carbons with same surface chemistries were tested. Below 1.2 nm micropore size, the textural parameters were found to be very important. No direct relationship between the surface area of meso-pores and the activity was

observed. In other words, textural parameters play a role up to 1.2 nm, and then the surface chemistry plays the major role.

In the reaction over activated carbon fibers²⁷, main reaction products were styrene and carbon oxides with smaller amounts of benzene, benzaldehyde, acetophenone, benzoic acid and coke. Non activated fibers were found to be not active. In this study, different materials with similar surface chemistry were investigated to explore the influence of textural properties on the catalytic activity. It was found that materials with very small micropores are not good as catalysts. Again, minimum pore size of 1.2 nm is required for a good catalyst.

Carbon nanotubes have attracted a great interest as well. Their activity was studied before and after oxidative treatment²⁶. Compared to activated carbons and graphites, they were found to exhibit the highest initial activity per initial surface area. Higher stability towards gasification was observed as well. Oxidized carbon nanotubes were more active than untreated samples during first minutes of reaction. Liquid oxidation was found to increase the amount of oxygen on the surface (in the form of carboxylic acids, lactones, carboxylic anhydrides, phenol and carbonyl), but without influencing the textural properties. Gas oxidation, on the other hand, increases the amount of surface oxygen and the specific surface area. With time on stream, coke deposition occurs and specific surface area becomes the key parameter.

Onion-like carbon is another candidate which was investigated²⁹. The steady state styrene yield at 790 K was compared to that obtained using graphites, industrial K-Fe catalyst and carbon nanofibers. Conversion levels up to 92 % after 2 hours of time on stream were observed. The function of OLC as a catalyst was uniquely related to its microstructure. This material was found to be superior to other forms of carbon in its catalytic activity. The reason for that was the higher number of active sites per unit weight and the optimized distribution of the oxygen-activating sites (basal planes) and Brønsted basic centers (prismatic planes).

Different nano carbon materials including carbon black, carbon nanotubes (CNT), onion-like carbons were compared in their catalytic activity in ODH of ethylbenzene²⁴. Onion-like carbon have shown the highest yield. Additionally, a reaction model was

proposed which involves carbonyl-quinone/hydroxyl and styrene/ethylbenzene as a redox couples.

The investigation of carbon materials as ODH catalysts revealed that in addition to the surface topography, surface chemistry (mainly the oxygen-containing groups on the surface) plays the most important role in determining the activity and behavior of the carbon material in the catalytic process. This fact promoted the extensive study and investigation of the surface chemistry and the correlation between the surface chemical environment and the catalytic activity of carbon materials.

2.3 Analysis of surface oxides on carbon

Qualification of surface oxides over carbon surfaces is of particular importance because of the high influence of these oxides on the properties of carbon materials. Different methods and approaches were used, including titration methods³⁰, infrared spectroscopy³¹, X-ray photoelectron spectroscopy^{28,31}, Thermal desorption spectroscopy^{19,20,31,32} and electrokinetic measurements³³.

In IR Spectroscopy³¹, absorption bands in the range of 1710-1750 cm^{-1} attributed to C=O stretching vibration indicate the presence of oxygen complexes. The wave numbers varied according to the oxidation method.

In studying the O 1s spectra using quasi in-situ XPS²⁸, a peak at 533.5 eV was assigned to hydroxyl or chemisorbed water, peak at 531.4 eV was assigned to carbonyl groups and a peak at 536.6 eV was claimed to be a charged peak. In a second study¹⁹ on activated carbons, following binding energies for O 1s were reported, 531.1 eV for quinone type, 532.3 eV for ether, phenol or carbonyl, 533.3 for anhydride, 354.2 eV for carboxylic acid and 535.9 eV for chemisorbed water.

Thermal desorption spectroscopy (TDS) has advantages like: the technique is easy and offers straightforward quantitative analysis of the desorbed species, in addition to being the most convenient way to study the thermal stability of surface oxides. Using this technique^{19,20,31,32} the following general trends were observed:-

- CO₂ forms from carboxylic acids at lower temperatures, or from lactones at higher temperatures.
- Carboxylic anhydrides form both CO and CO₂ peaks at the same time.
- Phenols, ether, and carbonyls produce CO peaks

The absolute positions of individual peaks vary widely between different laboratories.

In reviewing the different methods used for the qualification of oxygenated groups on the surface of carbon³⁰, it became clear that individual methods are not capable to identify the types of these groups.

Infrared spectroscopy is very difficult because of the strong IR absorption of carbon, although some progress was achieved by using Attenuated Total Reflectance (ATR) technique.

The thermal programmed desorption technique, although widely used, is not very well suited, and has high uncertainty. The desorption temperatures of the desorption peaks depend highly on the sample properties (pore size), the oxidation conditions, and the way TDS is carried out, in addition to the probability of secondary reactions of the evolved gases, especially in porous carbons. That's why the published TPD spectra differ widely. A sample of the reported desorption temperatures of some surface oxygenated groups on carbon materials is summarized in table 2.1

Lastly, in XPS, the differences in binding energy for different binding states are very small for an electronegative element like oxygen. Carbon atoms on the other hand, differ in their binding energy according to the way they bond to oxygen atoms. The technique, nevertheless, requires calibration because of charging problems. Thus, interpretation of results is normally not straight forward.

Accordingly, the use of single method is not recommended, but combination of more than one technique can offer better understanding.

Functional group	Desorbed species	T (K)	Ref.
Carboxylic	CO ₂	523 373-673 473-523	Otake et al. ³⁴ Zhuang et al. ³⁵ Zielke et al. ³⁶
Lactone	CO ₂	900 623-673 463-923	Zhuang et al. ³⁷ Zielke et al. ³⁶ Marchon et al. ^{24,32}
Carbonyl	CO	973-1253 1073-1173	Marchon et al. ³² Zielke et al. ³⁶
Anhydride	CO+CO ₂	900 623-673	Otake et al. ³⁴ , Zhuang et al. ³⁷ Zielke et al. ³⁶
Quinone	CO	973-1253 1073-1173	Marchon et al. ³² Zielke et al. ³⁶

Table 2.1 Reported desorption temperatures of oxygenated groups on carbon surface

2.4 Methodology

HOPG was chosen as a model catalyst. This material has advantages such as:

- a- It is absolutely metal-free: metals can interfere with the catalytic activity in addition to being known to catalyze carbon gasification.
- b- Non porous: this eliminates the diffusion difficulties
- c- It has well defined, renewable surface: the structure of this material is very ordered and well defined. In addition, new surface can be easily created many times by sample cleavage.
- d- High thermal stability and UHV suitability: this material is known to be very stable even at elevated temperatures, in addition to the absence of any degassing behavior that may complicate its use in UHV systems.

This material is composed of pure carbon which is (almost) free of any other elements. To be able to catalyze the ODH reactions, surface oxygen groups should be created (activation). Three ways were followed trying to create surface oxygen-functionality:-

- a- Heating in oxygen atmosphere at UHV conditions
- b- Sputtering with argon followed by exposure with oxygen

c- Sputtering with oxygen or a mixture of argon and oxygen

To recognize the nature of the activated HOPG, the chemistry of the surface was studied using AES, TPD and XPS. The morphology was studied using SEM and AFM.

The catalytic behavior of activated and non activated HOPG samples in the ODH of ethylbenzene was studied and compared to some other materials e.g. carbon nanotubes.

Lastly, the reacted samples were further investigated to have better understanding of the changing during reaction.

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