Introduction

Styrene, also known as vinyl benzene or cinnamene is an organic compound with the chemical formula C_8H_8. Under normal conditions, this aromatic hydrocarbon is an oily clear colorless liquid which evaporates easily and has a sweet smell.

Styrene is a key component in manufacturing a broad range of important materials which are used to make thousands of everyday products. The most recognizable material is polystyrene which was accidentally discovered by the German apothecary Eduard Simon In 1839. He isolated it by distillation of the natural balsam storax[1]. It was until 1930s when polystyrene was commercially produced and practically used by BASF in Germany and Dow chemicals in the USA. The World War II caused a large demand on the production of styrene which was used in producing synthetic styrene-butadiene rubber.

Being one of the least expensive thermoplastics on a cost-per-volume basis, Polystyrene is used nowadays in a wide range of fields and products such as packaging materials and housings for consumer products i.e. TV's and all kind of emerging products. It can be foamed to produce insulation boards, loose fill packaging and disposable food containers. Styrene-butadiene rubber (SBR) elastomers are used in passenger car tires and industrial hoses. Styrene-acrylonitrile copolymer (SAN) is used in drinking tumblers and battery cases, while acrylonitrile-butadiene styrene terpolymer (ABS) is used for piping and automotive components. Unsaturated polyester resins (UPR) which is better known as fiberglass is used in storage tanks, and simulated marble products.

Over 80 companies are now producing styrene monomer with an annual production of about 20 million tons.

Main commercial production routes[2]:

1- Ethylbenzene dehydrogenation over iron oxide-based catalysts.

$$\phi - CH_2 - CH_3 \xrightarrow{IronOxideCatalyst} \phi - CH = CH_2 + H_2 \quad \Delta H^0_{298\,K} = -124.3\ \text{KJ/mol}$$

This process accounts for about 85% of styrene world supply.

2- As a by-product in the epoxidation of propene with ethylbenzene and molybdenum complex-based catalysts. About 15 % of the world supply of styrene is made by this process.

3- Oxidative hydrogen removal by employing a noble metal catalyst that selectively oxidizes hydrogen. This method is originally named Styroplus, but known now as the SMART SM process. Although several licenses have been sold for this process, no corresponding plants are known to operate.

Although the majority of styrene is produced using the first route, this process encounters several draw backs including:-

- The need for high steam/oil ratio
- The reversibility of the process as a result of thermodynamic limitations and the need for product recycling in result.
- The process is highly endothermic and takes place at temperature as high as 600 ^{o}C.
- The used iron oxide-based catalyst suffers deactivation because of coking and leaching of the promoter.

In order to overcome the previously mentioned problems, the following alternative processes were proposed:-

- Oxidative dehydrogenation of ethylbenzene to utilize the exothermicity of this process which can be carried out at relatively lower temperature.

- Dehydrogenation of ethylbenzene followed by oxidation of the hydrogen aiming to supply the heat needed for the reaction from that produced by hydrogen oxidation and to shift the reaction equilibrium.

- Using membrane catalysts to shift the reaction equilibrium and carry out the reaction at lower temperature.

Among these methods, the oxidative dehydrogenation route was found to be promising and hence attracted a lot of interest during last decades. And among the many catalytic systems tested for this reaction, carbon materials found a great interest.

The main object of this work is to perform a model catalyst study of the oxidative dehydrogenation (ODH) of ethyl benzene over carbon materials, in the aim to explore the active centers and to understand the role of oxygen in this process. For that purpose, Highly Oriented Pyrolytic Graphite (HOPG) was utilized as a model catalyst and used to simulate the ODH reaction over other carbon materials.

Overview

The first chapter is a study of the surface termination of potassium-promoted Iron oxide thin films over Pt (111), in which Ion Scattering Spectroscopy was used to determine the surface termination of this model catalyst.

In the second chapter, some highlights from the literature dealing with the field of oxidative dehydrogenation over carbon materials and the surface chemistry of carbon materials used in this process is given.

In the third chapter, the used experimental methods and instrumentations are explained in addition to some details of the experiments' procedures.

The fourth chapter deals with the interaction of HOPG with oxygen and the production and investigation of oxygenated surface groups.

In the fifth chapter, the oxidative dehydrogenation experiments over HOPG and other materials are discussed.

In the sixth chapter, post-reaction investigations of different samples are explained and discussed.

The seventh chapter is a summary of conclusions.

(1) James, D. H.; Castor, W. M. In *Ullmann's Encyclopedia of Industrial Chemistry* 2000; Vol. a25, p 329.
(2) Cavani, F.; Trifir, F. *Applied Catalysis A: General* **1995**, *133*, 219-239.