

# OXIDATIVE DEHYDROGENATION OF ETHYLBENZENE TO STYRENE ON ACTIVATED CARBONS DERIVED FROM A NATIVE WOOD AS CATALYST

J.P. de CELIS<sup>†‡</sup>, M.S. VILLAYERDE, A.L. CUKIERMAN<sup>‡</sup> and N.E. AMADEO<sup>†</sup>

<sup>†</sup> Laboratorio de procesos Catalíticos. Dto. de Ing. Química. Facultad de Ingeniería. Universidad de Buenos Aires.

E-mail: norma@di.fcen.uba.ar

<sup>‡</sup> Programa de Investigación y Desarrollo de Fuentes Alternativas de Materias Primas y Energía - PINMATE- Dto. de Industrias. Facultad de Ciencias Exactas y Naturales. Universidad de Buenos Aires, Pabellón de Industrias, Intendente Güiraldes 2620, Ciudad Universitaria, (C1428BGA) Buenos Aires, Argentina.

**Abstract**— Activated carbons were developed by phosphoric acid activation of a native wood (*Prosopis ruscifolia*) under a self-generated atmosphere or flowing air. Their potentiality as catalyst for oxidative dehydrogenation of ethylbenzene to styrene was examined at pre-established operating conditions. The carbons developed in the self-generated atmosphere showed specific surface area of 2281 m<sup>2</sup>/g and total pore volume of 1.7 cm<sup>3</sup>/g, whereas values of 1638 m<sup>2</sup>/g and 1.3 cm<sup>3</sup>/g, respectively, characterized those obtained in air. A commercial activated carbon (1200 m<sup>2</sup>/g and 0.7 cm<sup>3</sup>/g) was also used for comparison. Both wood-derived carbons resulted potentially suitable as catalyst for ethylbenzene oxidative dehydrogenation. Nevertheless, those developed in the self-generated atmosphere showed a better catalytic performance than the carbons obtained in air and the commercial sample. The behaviour could be due to its lower microporosity compared with the commercial sample, and to the formation of oxidative condensation products during the oxidative dehydrogenation of ethylbenzene with greater content of carbonyl groups than for the sample activated under flowing air. Chemical and textural characterization of the used carbons conclusively evidenced the presence of oxidative condensation products pointing to formation of new active surfaces.

**Keywords**— ethylbenzene, styrene, oxidative dehydrogenation, activated carbons, catalyst.

## I. INTRODUCTION

Styrene (ST) is one of the most important basic chemical species. It is mainly used as the monomer of synthetic polymers. It is commercially produced by the dehydrogenation of ethylbenzene (EB) on iron oxide catalyst at 873-973K. However, the dehydrogenation of EB is thermodynamically limited and a very energy consuming process because of the excessive requirement of superheated steam. As an alternative, the oxidative dehydrogenation (ODH) of EB has been proposed as it is free from thermodynamic limitations regarding conversion, and it operates at lower temperatures involving exothermic reactions. Most of the work on EB has been devoted to the selection of suitable catalysts and appropriate reaction conditions to improve the styrene yield and selectivity (Morales and Lunsford, 1989; Swaan *et al.*, 1992; Chang *et al.*, 1993; Sulikowski *et al.*, 1994).

It has been reported that high activities and selectivity can be obtained at relatively low temperature using activated carbon as catalyst (Pereira *et al.*, 1999; Pereira *et al.*, 2000). In previous works (Iwasawa *et al.*, 1973; Schraut *et al.*, 1987; Cadus *et al.*, 1990), it has been concluded that oxygenated functional groups on catalyst surface, especially quinone-like structures, enhance the catalytic performance. Considering that the textural properties and surface functional groups of activated carbons (ACs) depend on the precursor used, as well as on the strategy and preparation conditions (Patrick, 1995), we have studied the feasibility of developing ACs with specific characteristics for their use as catalyst in ODH (de Celis, 2003).

In the present work, activated carbons have been developed from *Prosopis ruscifolia* wood as a precursor through the chemical activation process with phosphoric acid solution as the activating agent for two different activation atmospheres and pre-established experimental conditions. In this sense, the aim of this paper is to study the influence of the activation atmosphere on textural properties, chemical characteristics and catalytic behaviour of the resulting ACs in EB oxidative dehydrogenation. For the sake of comparison, a commercial activated carbon (CAC) was also characterized and catalytically evaluated.

## II. MATERIALS AND METHODS

### A. Preparation of the Activated Carbons (ACs)

*Prosopis ruscifolia* is a species of tree indigenous to south of South America. It grows very rapidly in Chaco region, the vast plain in Argentina, Paraguay, and Bolivia. Until a few years ago, it was considered as a plague due to its ability to fast invade degraded lands turning them unproductive. A recent programme has been launched in order to control the spread of this species, and *Prosopis* wood has been introduced in the market for furniture manufacture and the timber industry.

A piece of *Prosopis ruscifolia* wood without bark kindly provided by GESER (Facultad Ciencias Exactas y Naturales, Universidad de Buenos Aires) was used for ACs preparation. It was crushed, milled, and screen-sieved. Fractions of average particle diameter of 0.75 mm were employed to obtain the ACs.

Briefly, the sawdust was impregnated with a H<sub>3</sub>PO<sub>4</sub> acid aqueous solution (50 % wt), using an acid/precursor weight ratio of 2. Each impregnated sample was placed