# Production of Ethylene from Ethanol Dehydration over $H_3PO_4$-Modified Cerium Oxide Catalyst

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Production of ethylene from ethanol dehydration was investigated over $H_3PO_4$ (10wt% to 30wt%)-modified cerium oxide catalysts synthesized by wet impregnation technique. The prepared catalysts were characterized using scanning electron microscope (SEM), $N_2$ adsorption-desorption method, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) for the physicochemical properties. The ethanol catalytic dehydration was carried out in a fixed-bed reactor at 673-773 K and at ethanol partial pressure of 33 kPa. The effects of phosphorus loading on catalyst and reaction temperatures were investigated in terms of catalytic activity towards product selectivity and yield. Overall, the selectivity and yield of ethylene increased with the temperature and phosphorus loading. The highest ethylene selectivity and yield were 99% and 65%, respectively, at 773 K and 33 kPa over the 30wt% $H_3PO_4$-modified cerium oxide.

*Keywords:* ethylene production, ethanol dehydration, $H_3PO_4$ modification, cerium oxide

## 1. INTRODUCTION

The increasing demand of ethylene is due to its uses in producing polyethylene, one of the primary components in the most of the plastic and in petrochemical industry [1]. Besides that, ethylene acts as precursors for surfactant chemicals such as ethylene oxide or ethylene glycol. With increased demand, global ethylene production has grown at an average rate of almost 4.5% per year from 2009-2014. Currently steam cracking of hydrocarbon from fossil fuel is still dominating the production market because of the high production cost and energy consumption associated with catalytic dehydration pathway. Due to the increasing demands for energy, stricter environmental regulations, and continued depletion of fossil feedstock, alternative and renewable energy resources have attracted increased interest in recent research. In the view of potential limitations of ethylene availability from the current sources, catalytic dehydration of ethanol (especially bioethanol) to ethylene has become a completely renewable process for producing ethylene [2].

Ethanol dehydration is a process in which water molecules are removed, or the equivalent of water molecules removed from ethanol to produce ethylene when heated together with catalyst. There are two reactions that occur in parallel during catalytic dehydration of ethanol as in Eqns. (1) to (2):

$$C_2H_5OH \leftrightarrow C_2H_4 + H_2O \qquad +44.9 \text{ kJ/mol} \qquad (1)$$

$$2C_2H_5OH \leftrightarrow C_2H_5OC_2H_5 + H_2O \qquad -25.1 \text{ kJ/mol} \qquad (2)$$

The low temperature favors the side reaction to produce diethyl ether; in contrast, higher reaction temperature is theoretically favoring the main reaction (ethanol dehydration). The dehydration reaction is endothermic and need 390 calories per gram of ethylene produced. The temperature of diethyl ether formation is mainly between 423 K and 573 K, while ethylene formation is favoured between 593 K and 773 K.

Acidic catalysts are often used in ethylene production from ethanol dehydration. The traditional homogeneous catalysts used are sulfuric acid or phosphoric acid in almost all industrial scale processes. The former usually requires higher reaction temperatures and yields lower ethylene selectivity [3]. Due to the low yield and byproducts formation, sulfuric acid and phosphoric acid have been replaced by heterogeneous catalysts such as alumina.

Many studies have been carried out with different technologies and using various acidic heterogeneous catalysts such as alumina, silica, zeolites, metal oxides and heteropolyacids [4-7]. Among those studied catalysts, gamma alumina ($\gamma$-$Al_2O_3$) and HZSM-5 zeolite have drawn the most attention for their high activity and selectivity. HZSM-5 has been widely used in alcohol dehydration reactions due to its uniform pore structure, high surface area, and adjustable acidity. Low reaction temperature (>473 K) favors the reaction towards ethylene production from ethanol dehydration over HZSM-5. HZSM-5 can achieve 60-