

Research article

Catalytic ethylene production from ethanol dehydration over non-modified and phosphoric acid modified Zeolite H-Y (80) catalysts



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ABSTRACT

The present work reports on the effects of phosphoric acid-modified Zeolite-Y towards ethylene formation from ethanol dehydration. The catalyst was impregnated with different H₃PO₄ loadings from 10 to 30 wt%. All the catalysts were characterized using N₂-physisorption, thermogravimetric analysis, NH₃-TPD, FTIR, SEM-EDX, X-ray diffraction and XPS techniques. The non-modified Zeolite-Y with Si/Al 80:1, H-Y (80) was found to exhibit excellent catalytic activity owing to the presence of weak acid sites that was able to protonate the hydroxyl group of ethanol. Although ethanol conversion dropped with phosphorus modified catalysts, it was found that the modified Zeolite-Y with 10 wt% H₃PO₄ can achieve 99% selectivity to ethylene at 723 K and ethanol partial pressure of 16 kPa. Overall, ethanol conversion and ethylene selectivity decreased in the order of H-Y (80) > 10P/H-Y (80) > 20P/H-Y (80) > 30P/H-Y (80). The decrease in ethanol dehydration activity of phosphorus modified catalysts can be ascribed to the reduced BET specific surface area and pore volume due to the surface coverage by layers of H₃PO₄, consequently, hindering ethanol access to the active site. However, the spent phosphorus modified Zeolite-Y catalyst consistently showed less carbon formation compared to the undoped catalyst. This could be due to the reduction in strong acid sites and also hindering of C₂H₅OH from travelling deep into the pore networks of H-Y (80), therefore reducing the residence time with the consequence of minimizing the carbon laydown.

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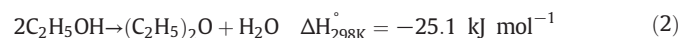
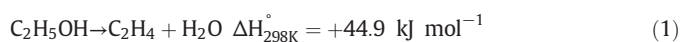
1. Introduction

Ethylene is an essential precursor or intermediate in the chemical industry. It serves as the monomer for the synthesis of polyethylene, a material that is widely employed for the production of films for packaging, via polymerization. Significantly, polyethylene (low density polyethylene (LDPE) and high density polyethylene (HDPE)) is the world's most widely used plastic and this process alone consumes up to half of the ethylene produced [1]. The demand for polyethylene in the chemical industry outstrips other polymers, i.e. polypropylene and polyvinyl chloride [2].

Conventionally, commercial production of ethylene is via thermal steam cracking of petroleum hydrocarbon feedstocks such as naphtha from the crude distillation column [3]. Naphtha is a mixture of C₅ to C₁₀ hydrocarbons which can be obtained from the distillation of crude oil. The cracking process usually requires >873 K process temperature and it produces lower ethylene yield compared to catalytic dehydration

of ethanol [4]. A steam cracker is one of the most technically complex and energy intensive plants in the chemical industry. Although the cost of production is continually reduced by improvements made in energy efficiency of the furnace, the harsh operating conditions i.e. high temperature and pressure, have not changed. In addition, naphtha hydrocarbon is obtained from a finite source which is unfortunately dwindling.

Dehydration of ethanol therefore serves as an alternative technology to synthesize this important compound, ethylene. There are two competitive pathways for catalytic dehydration of ethanol to ethylene, viz. the intramolecular dehydration of ethanol to ethylene which is endothermic; and intermolecular dehydration of ethanol to diethyl ether which is exothermic as shown in both Eqs. (1) and (2).



These two reactions can occur in parallel during catalytic dehydration of ethanol. Consequently high temperature is more favorable to produce ethylene while low reaction temperature prefers the formation of diethyl ether [5,6].

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The earliest material employed as the catalyst is alumina. Indeed, alumina is the most widely reported catalyst in ethanol dehydration. For example, a study conducted by Phung et al. [7] showed that a total conversion (100%) of ethanol can be achieved over pure Al_2O_3 with selectivity to ethylene attaining 99%. It is posited that the presence of Lewis acid sites as an activity center on an alumina surface assists a dissociative adsorption of ethanol. However, the major drawback of this catalyst is its poor stability i.e. after reaction for 80 h, the yield of ethylene decreased from 82.8% to 62.1% [4]. Another study has shown that alumina doped with manganese oxide and iron (II) oxide can only achieve ethanol conversion of ~20.5 to ~59.7% when reaction temperature was increased from 473 K to 723 K [8].

Zeolite of different classes are initially employed in the catalytic reactions involving hydrocarbons [9–12]. Recently, there are voluminous publications on the use of zeolites as catalyst for ethanol dehydration into ethylene, with most of the studies centered on the H-ZSM-5 zeolite [13–16]. Zeolites possess superior catalyzing ability, but it easily succumbs to physical deactivation via carbon deposition. Therefore, zeolites are always modified with transition metal oxides to reduce coke deposition and enhance its stability. For instance, Zhan et al. [17] have modified H-ZSM-5 with phosphorus and lanthanum. With 0.5%La-2%PH-ZSM-5, there was a total ethanol conversion and 99% of ethylene selectivity. In another separate work, microporous H-ZSM-5 zeolite was post treated by desilication with sodium hydroxide and dealumination with oxalic acid as reported in [15]. This treatment has successfully increased the weak acid sites and culminates in a better catalytic performance compared to the parent catalyst.

On the other hand, there are very few studies in the open literature on the use of Zeolite-Y for catalyzing ethanol dehydration. Zeolite-Y catalysts are those with Si:Al ratios of >2.2 [18]. The crystals of Zeolite-Y consist of frameworks with SiO_4 and AlO_4 tetrahedrons crosslinked by sharing oxygen atoms, with a chemical formula of $0.9 \pm 0.2\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:w\text{SiO}_2:x\text{H}_2\text{O}$, wherein w is a value >3 , up to about 6 while x represents values of up to about 9 [19]. Zeolite-Y is mainly used in the industries for adsorption purposes due to its high heat resistance and with a pore size larger than the dimensions of ethanol molecules [20]. Previous research on Zeolite-Y with a Si:Al ratio of 5.1:1 showed that the ethanol conversion using this catalyst was relatively low, 1.7% compared to other zeolites (H-FER and H-MFI), due to a lesser number of weak and strong Lewis acid sites [21]. However, to the authors' best knowledge, there has been no report on phosphorus modified Zeolite-Y for ethanol dehydration into ethylene. Thus, Zeolite-Y was chosen to study over catalytic ethanol dehydration due to the specific zeolite configuration with large open pores that can be an effective pathway for the reaction to occur. Nonetheless, there is no systematic study that reports on the effects of Zeolite-Y and phosphorus modified Zeolite-Y in catalytic ethanol dehydration. Hence, the non-modified Zeolite-Y and phosphorus modified Zeolite-Y were employed to study the effects of reaction temperature and ethanol partial pressure in the current work. The fresh and spent catalysts were characterized by various techniques, viz. scanning electron microscopy with energy dispersive spectrometer (SEM-EDX), X-ray diffraction (XRD), Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), N_2 physisorption, temperature programmed desorption of ammonia (NH_3 -TPD) and also thermal profiles via thermogravimetric analysis (TGA).

2. Experimental section

2.1. Materials

Zeolite-Y, H-Y (80) with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 80:1$ was purchased from Zeolyst, United States of America. Absolute ethanol and 85 wt% phosphoric acid were purchased from Merck, United States of America. Distilled water from Aqua Matic AEC/8S, was obtained readily from the laboratory of Universiti Malaysia Pahang.

2.2. Catalyst preparation

The non-modified Zeolite-Y catalyst was used as received. The modified phosphorus Zeolite-Y (Si/Al ratio = 80:1) was prepared by mixing the zeolite with the purchased 85 wt% phosphoric acid (H_3PO_4). This method involved the addition of a calculated quantity of zeolite into the acid solution followed by thorough stirring, drying and thermal-treatment. For 10 wt% H_3PO_4 /Zeolite-Y, a batch of 10 g catalyst was prepared by adding 9 g of Zeolite-Y and 1.2 g of H_3PO_4 and the resulting mixture was added with 40 ml of distilled water to ensure homogenation of the solution. The solution was then magnetic-stirred for 3 h under ambient condition followed by drying in an oven (Memmert UFE-500) for 12 h at 373 K. During the first 6 h of the drying process, the catalyst was manually stirred using a glass rod for each hour to maintain a relative homogeneity of the slurry. After 12 h, the dried catalyst was transferred to a muffle furnace (Carbolite AAF11/3), and was thermally treated for 5 h at 773 K employing a heating rate of 5 K min^{-1} . The catalyst was then cooled to room temperature and ground for physicochemical characterization and reaction studies. The steps were repeated for 20 wt% and 30 wt% H_3PO_4 -doped Zeolite-Y; loading of H_3PO_4 acid was capped at 30 wt% because higher loading has altered the structural appearance of Zeolite-Y.

2.3. Catalyst characterization

N_2 physisorption was carried out by using a Thermo Scientific Surfer employing the mesopores method with approximately 0.3 g of catalyst for each analysis. The sample was heated to 573 K and then left overnight to remove any moisture and volatile impurities. Subsequently, the sample was transferred to an analyzer for N_2 physisorption at 77 K. The total specific surface area of the catalyst was calculated using the Brunauer-Emmett-Teller (BET) isotherm method while the pore volume and average pore diameter were estimated using the Barrett-Joyner-Halenda (BJH) correlation.

Ammonia temperature-programmed desorption (NH_3 -TPD) was carried out in a Thermo Finnigan TPDRO 1100. The catalyst was pretreated with N_2 at 423 K for 15 min. The adsorption of NH_3 was carried out at room temperature for 45 min and after saturation was achieved, N_2 was purged in to eliminate the remaining NH_3 gas. Analysis of desorption of NH_3 was done under the flow of helium at temperatures ranging from 323 K to 1273 K at a rate of 10 K min^{-1} .

Thermogravimetric analysis (TGA) was performed using a Hitachi STA7200 with approximately 50 mg of catalyst employing a heating rate of 10 K min^{-1} , to bring the temperature from room temperature to 1073 K under an N_2 -blanket for fresh catalysts and high purity air for the used catalysts.

The surface morphology, particle distribution and elemental analysis were studied using scanning electron microscopy with X-ray analysis (SEM-EDX) of a Hitachi TM3030Plus brand with an accelerating voltage of 20 kV.

The Fourier transform infrared spectroscopy (FTIR) of catalysts was carried out in a Thermo Nicolet iS50 over the wavenumber that ranged $4000\text{--}400 \text{ cm}^{-1}$ to determine the functional groups present in the sample. The result from this analysis can be used to predict the chemical properties of the catalysts.

The X-ray diffraction (XRD) instrument employed was a Rigaku Miniflex II with $\text{CuK}\alpha$ radiation and Ni filter, operated in the vertical mode on 30 kV and 15 mA. The pattern recorded was ranging from 3° to 80° at a scan rate of 2° min^{-1} . The mean size of crystallites, d_p , of each sample was estimated using the Scherrer equation shown in Eq. (3).

$$d_p = \frac{K \times \lambda}{\beta \cos \theta} \quad (3)$$

whereby d_p is the crystallite size in nm, λ is wavelength of X-ray (0.154 nm), β is the line broadening at half maximum intensity

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