Liquid-phase dehydration of 1-phenylethanol on solid acids: Influence of catalyst acidity and pore structure

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ABSTRACT

The liquid-phase dehydration of 1-phenylethanol (PHE) over different solid acids was studied at 363 K using cyclohexane as solvent. It was found that the catalyst activity and selectivity strongly depended on: (1) the nature, strength and density of acid sites and (2) the textural properties of the catalyst.

Catalysts containing mainly surface Brønsted acid sites of medium–high strength, such as Amberlyst 15, HPA/SiO$_2$, and HMOR zeolite, showed low initial styrene (STY) selectivity because the PHE dehydrated to alpha-methylbenzyl ether (AME) at higher or similar rates than to STY. Both primary products, STY and AME, were consecutively transformed to other heavy products (HP).

Catalysts containing predominantly Lewis acid sites, such as ZnO/SiO$_2$, Al-MCM-41 and SiO$_2$–Al$_2$O$_3$, selectively transformed PHE to AME. The ether can be sequentially converted to STY and HP, depending on the solid acidity. Solid acids having strong surface Lewis sites, e.g. SiO$_2$–Al$_2$O$_3$, showed high dehydration rate and HP production. Samples containing exclusively weak Lewis acid sites, e.g. γ-Al$_2$O$_3$, were not active in the PHE dehydration at 363 K.

Only zeolites HZSM-5, HBEA and HY, with similar surface density of Brønsted and Lewis acid sites, converted selectively PHE into STY, giving initial STY selectivities between 83 and 96%. However, HY zeolite was rapidly deactivated due to the blockage of its microporous structure by bulky compounds formed inside the large cages of 13 Å. Instead, on HBEA, STY was converted to HP that can diffuse through the solid microporous structure. Then, the selectivity to STY was drastically reduced with time. A constant and high STY selectivity at total PHE conversion was only obtained with HZSM-5. The pore size of this zeolite is enough to allow the diffusion and conversion of PHE into STY, but it is not adequate to form the surface intermediates leading to AME and HP.

Thus, it was proved that: (1) the surface Brønsted to Lewis ratio strongly influences the initial selectivity in the liquid-phase PHE dehydration; (2) a similar Brønsted to Lewis ratio on the solid acid surface is necessary to obtain high initial selectivity to STY; and (3) the right porous structure is crucial to avoid HP production and keep constant the STY selectivity at high PHE conversion. From the experimental results obtained in this work, a mechanistic approach was proposed in order to explain the influence of both acid site nature and pore size on the selective PHE dehydration in liquid phase.

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1. Introduction

One powerful and usual method to obtain olefins in the chemical industry is the alcohol dehydration, which can be performed in either gas or liquid phase. On the one hand, gas phase dehydration of alcohols is a relatively benign process for the environment that was traditionally carried out using titania [1], alumina [2–4], silica–alumina [5] or zeolites [6,7] as catalysts, at temperatures higher than 473 K. On the other hand, liquid-phase alcohol dehydration is generally carried out using traditional homogeneous catalysis, comprising strong acids such as H$_2$SO$_4$, KHSO$_4$, H$_3$PO$_4$ or p-toluensulfonic acid [8–10]. This technology has severe drawbacks during both chemical reaction and catalyst recovering-reuse, such as generation of large amount of byproducts, high energy demand, serious corrosion in equipments and environmental problems due to catalyst leakages [11]. Consequently, it is of great importance to find new active and selective catalysts for eco-friendly liquid-phase alcohol dehydration. The main advantages of heterogeneous catalysis over its homogeneous counterpart are: (1) reduced equipment corrosion; (2) easy product and catalyst separation; (3) low-cost recycle of catalysts; and (4) less contamination in waste streams due to leakages of catalyst. Thus, heterogeneous catalysis offer relevant possibilities for sustainable olefin

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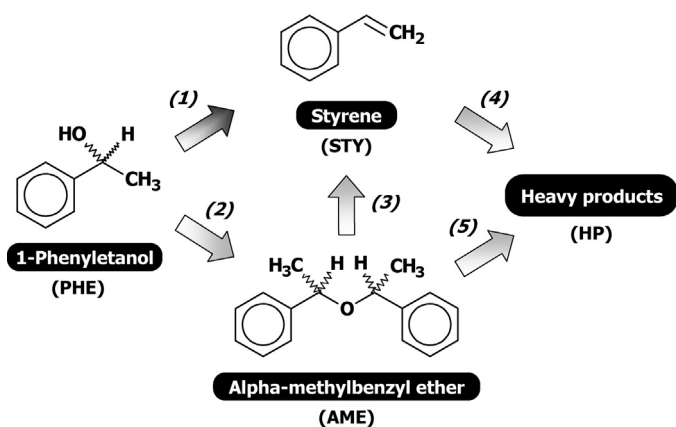
Fig. 1. Reaction scheme for the 1-phenylethanol dehydration over acidic catalysts.

production, replacing environmental hazardous homogeneous catalysis by processes that use solid acid catalysts [11,12].

In particular, intramolecular dehydration of 1-phenylethanol (PHE), a secondary aromatic alcohol, is of industrial interest in order to produce styrene (STY). This is a well-known reaction, because 15% of the worldwide STY is produced by PHE dehydration, which is a byproduct obtained in the production of propylene oxide [13]. The PHE dehydration process is the most used when high purity STY is needed [5]. This olefin is used as raw material for the production of a wide variety of polymeric products, specially thermoplastics and elastomers, to produce goods such as furnitures, tanks, toys, etc. [14]. The liquid-phase PHE dehydration is also used as test reaction for the synthesis of fine chemicals, such as indenes from indanols, widely used for the production of pharmaceuticals and polymerization catalysts [15–18]. Besides STY, and depending on the catalyst and operational conditions, alpha-methylbenzyl ether (AME) can also be a primary product formed through intermolecular PHE dehydration (Fig. 1). Both AME and STY can lead consecutively to the formation of heavy products (HP) over acidic catalysts.

PHE dehydration in liquid phase using solid catalysts such as Al_2O_3, $SiO_2-Al_2O_3$, zeolites or acidic resins have been reported in previous works [19–24]. In all the cases, the reaction temperature was always higher than 423 K. In general, selectivity to STY was between 74 and 98%, depending on the experimental conditions, though some deactivation of the catalyst took place. Lange and Otten studied the PHE dehydration under reactive distillation conditions over microporous and mesoporous solid acids at 443 K [22,23]. These authors remarked the importance of the shape selectivity for obtaining high STY selectivity and observed important deactivation of the catalysts. Recently, Pérez Valencia et al. reported the selective 1-phenylethanol dehydration at temperatures between 398 and 460 K using 1-methylimidazolium hydrogen sulfate as catalyst in a bubble column reactor [25]. Only few papers dealing with the liquid-phase dehydration of PHE at temperature lower than 373 K have been published [26–28]. Tarlani et al. dehydrated PHE at 353 K over $H_6P_2W_{12}O_{62}$ using dichloroethylene as solvent, but they obtained mostly HP and only traces of STY [26]. In previous works, we have reported the successful use of zeolites for the selective PHE liquid-phase dehydration at 363 K [27,28]. Dealuminated mordenite-like zeolites were more selective to STY than to AME, though their microporous structure allows the formation of bulky products [27]. On the other hand, STY selectivities higher than 92% were obtained over HZSM-5 and a mechanistic LHHW kinetic model was proposed to interpret the results [28]. On the basis of the information found in the open literature, it was concluded that a more systematic and exhaustive

study is necessary in order to explain the very changing selectivity to styrene obtained with the different solid acids mentioned above.

From an industrial point of view, the successful use of solid acid catalysts for eco-friendly processes is based on the understanding of the influence of both acid and textural properties on the selectivity. To our knowledge, there is very little information in the open literature in which the influence of acidity and pore structure on the selective liquid-phase PHE dehydration under mild conditions was studied. In this work the liquid-phase dehydration of PHE was carried out at 363 K using cyclohexane as solvent, employing several selected acidic solids having different nature, strength and density of acid sites and with markedly different textural properties. The aim is to investigate the influence of acidity and porous structure on the PHE dehydration rate and selectivity to STY. To achieve this aim, mesoporous and microporous solids belonging to one of the following three categories were employed as catalysts for the liquid-phase PHE dehydration: (1) solid acids having mainly surface Lewis acid sites; (2) solid acids having mainly surface Brønsted acid sites; (3) solid acids having similar proportions of Brønsted and Lewis acid sites on the surface. It was found out that high initial selectivity to STY is obtained only when solids with similar surface concentrations of Lewis and Brønsted acid sites are used as catalysts. However, this high selectivity was preserved only if the pore size is such that conversion of STY into HP can be inhibited. On the basis of the experimental results obtained in this work, a mechanistic approach was finally proposed in order to explain the influence of both acid site nature and pore size on the selective PHE dehydration in liquid phase. The final goal is to determine the requirements to perform an eco-friendly and sustainable olefin production from a selective alcohol dehydration under mild conditions.

2. Experimental

2.1. Catalyst preparation

HPA/SiO_2 and ZnO/SiO_2 catalysts were prepared by incipient wetness impregnation of commercial SiO_2 (Grace G62, 99.7%, $S_g = 230 \, m^2/g$, $V_P = 0.49 \, cm^3/g$) with aqueous solutions of $H_3PW_{12}O_{40}$ (99%, Merck) and $ZnCl_2$ (99.5%, Aldrich), respectively. The impregnated precursors were dried at 373 K for 12 h and then calcined for 2 h in air at 573 K (HPA/SiO_2) or 623 K (ZnO/SiO_2). The HPA and ZnO loadings were 28 and 20%, respectively.

Al-MCM-41 sample was synthesized by the sol–gel method, according to Edler and White [29]. Sodium silicate solution (14% NaOH and 27% SiO_2, Aldrich), cetyltrimethylammonium bromide (Aldrich), aluminum isopropoxide (Aldrich), and deionizated water were used as the reagents. The composition of the synthesis gel was $7SiO_2-xAl_2O_3-2.7Na_2O-3.7CTMABr-1000H_2O$. The pH was adjusted to 10 using a 0.1 M H_2SO_4 solution, and then the gel was transferred to a Teflon-lined stainless-steel autoclave and heated to 373 K in an oven for 96 h. After crystallization, the solid was washed with deionizated water, dried at 373 K and finally calcined in air at 773 K.

Commercial Amberlyst 15 resin (Rohm and Haas, $37 \, m^2/g$) was treated in N_2 at 373 K for 8 h before using in the catalytic tests. Amberlyst 15 is a well-known resin based on polystyrene, cross-linked with divinylbenzene (DVB) and sulfonated at a level equivalent to one sulfonic acid group per STY/DVB unit [30]. HY zeolite was obtained by triple ion exchange of a commercial NaY zeolite (UOP-Y54) with an 1 M aqueous solution of NH_4Cl at 353 K in a rotavapor during 2 h and subsequent calcination in air at 773 K. Commercial zeolites HZSM-5 (Zeocat Pentasil PZ-2/54, 0.43 wt.% Na), HMOR (Zeocat HZM-760), HBEA (Zeocat PB), $SiO_2-Al_2O_3$ (Ketjen LALPV) and γ-Al_2O_3 (Ketjen CK-300) samples were calcined in a dried air flow at 773 K before performing any characterization and catalytic tests.