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Effects of added phosphorus on conversion of ethanol to propylene over ZSM-5 catalysts

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ABSTRACT

We investigated the effects of added phosphorus on the conversion of ethanol to propylene over ZSM-5 zeolite catalysts. We found that the activity of the catalysts was enhanced by the addition of phosphorus, and we suggest that the added phosphorus suppressed oligomerization of propylene and butene by decreasing the acidity of the active sites of the zeolites. Furthermore, the addition of phosphorus greatly enhanced the hydrothermal stability of the zeolites and thus substantially improved the catalyst durability during ethanol conversion. Carbon deposition, which was the main cause of deactivation of the phosphorus-modified zeolites, was suppressed by H_2O produced by dehydration of ethanol.

1. Introduction

In view of the impending shortage of petroleum and the need to minimize CO_2 emissions, finding alternatives to petroleum has become a high priority worldwide. One of the best alternatives is biomass because it is an abundant and carbon-neutral renewable resource. Biomass (which includes agricultural crops and wastes, forestry residues, aquatic plants, and animal and municipal wastes [1]), can be combusted directly to generate heat and electricity and can be thermochemically or biochemically converted to combustible liquids (e.g., bio-oils, methanol, and ethanol) and gases (e.g., methane and hydrogen) [2]. For example, bioethanol is readily obtained by fermentation, which is one of the most commonly used biochemical conversion processes, of biomass feedstocks such as sugarcane, sugar beet, and starch crops (mainly corn and wheat). In 2006, total world production of bioethanol reached 51.3 billion liters [3]. Today, bioethanol is utilized mainly as a fuel or fuel additive in motor vehicles.

Recently, the use of bioethanol as a feedstock in the chemical industry has received attention. For example, the catalytic dehydration of ethanol yields ethylene, a basic product for many applications in the petrochemical industry. The main catalyst used for this process is pure or doped alumina [4]. In 2007, Braskem announced that it would start the large-scale manufacture of polyethylene from bioethanol [5].

Propylene is another important feedstock in the chemical industry, and the demand for propylene is growing much faster than that for ethylene because of the need for propylene derivatives such as polypropylene and propylene oxide [6]. Therefore, the development of processes for production of propylene from bioethanol has attracted considerable attention.

Catalytic conversion of ethanol to propylene over zeolites has been reported [7–14]. Zeolites with an 8-membered-ring pore system, such as SAPO-34 [7] and LEV [8], selectively convert ethanol to propylene. However, these zeolites are rapidly deactivated by carbon deposition. Makarfi et al. [9] studied the effect of the Si/Al ratio on the activity and selectivity of H-ZSM-5 zeolites for conversion of bioethanol to propylene and observed that the formation of C_3–C_4 hydrocarbons depends on the Si/Al ratio. Aguayo et al. [10] studied the effect of operating variables on the catalytic transformation of ethanol into hydrocarbons over ZSM-5 zeolites. Xia et al. [11] found that acidic sites on ZSM-5 zeolites were the active sites for conversion of ethanol to propylene and that the acidity and reactivity of the active sites were the same for ZSM-5 zeolites with different Si/Al_2 ratios. The catalytic activity was proportional to the number of acidic sites.

Various investigators have studied the modification of ZSM-5 zeolites with metals such as Fe [12] or W and La [13] to improve propylene selectivity. Because zeolites are irreversibly deactivated during the reaction, investigations have been conducted with the goal of improving catalyst stability. The hydrothermal stability of zeolites is enhanced by the addition of phosphorus [14–20], and the role of the added phosphorus in the stability enhancement has been investigated by several research groups [17–20]. Recently, we reported that phosphorus-modified ZSM-5 (P-ZSM-5) catalysts

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