Applied Catalysis A: General 417–418 (2012) 137–144

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Conversion of ethanol to propylene over HZSM-5(Ga) co-modified with lanthanum and phosphorous

Yoshiyasu Furumoto, Nao Tsunoji, Yusuke Ide, Masahiro Sadakane, Tsuneji Sano*

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

ARTICLE INFO

Article history:
Received 16 November 2011
Received in revised form
17 December 2011
Accepted 20 December 2011
Available online 30 December 2011

Keywords:
Ethanol
Propylene
ZSM-5
Phosphorous
Lanthanum

ABSTRACT

Conversion of ethanol to propylene was carried out over HZSM-5(Ga) co-modified with lanthanum and phosphorous (La/P/HZSM-5(Ga)). The propylene yield was strongly dependent on both the La/Ga and P/Ga ratios, and the highest value of ca. 29 C-% was obtained at a P/Ga ratio of 1 and a La/Ga ratio of 0.4. FT-IR, ^{31}P MAS NMR, and ^{71}Ga MAS NMR measurements demonstrate that the introduced lanthanum reacts with the pre-introduced phosphorous to regenerate some of Brønsted acid sites (Si(OH)Ga), and accordingly, the Brønsted acid sites are homogeneously distributed within the zeolite framework. In addition, the catalytic stability as well as the catalytic activity of HZSM-5(Ga) was effectively enhanced by co-modification with lanthanum and phosphorous because of the suppression of carbonaceous deposition and elimination of gallium from the zeolite framework.

1. Introduction

Owing to the increasing concerns about global warming and exhaustion of petroleum resources in recent years, the production of light olefins such as ethylene and propylene from bio-ethanol obtained by fermentation of biomass has attracted considerable attention. Light olefins are basic raw materials used in the synthesis of various chemicals and are generally produced by steam cracking of naphtha. There are many reports concerning the production of hydrocarbons such as ethylene, gasoline, and aromatics from ethanol, aqueous ethanol and bio-ethanol using solid catalysts such as zeolites [1–13]. However, there are few reports on the transformation of ethanol to propylene [14–21]. Literature reports presented thus far indicate that the distribution of products obtained in the zeolitic ethanol conversion process is strongly dependent on the acidity (acid strength and number of acid sites) as well as the channel structure of the zeolites. Therefore, significant effort has been devoted to controlling the acidity of zeolites by modifying them with a variety of metals including Zr, La, Sr, and P. Several structural models of the acid sites have been proposed for the zeolites modified with these metals, particularly with phosphorous [22–25].

We prepared isomorphously framework-substituted ZSM-5 zeolites (HZSM-5(M), M = Al, Ga, and Fe) having different acid strengths and investigated their catalytic performance in the conversion of ethanol to propylene [26]. High propylene yields were obtained over HZSM-5(Ga) and HZSM-5(Al), and the hydrothermal stability of HZSM-5(Ga) was found to be higher than that of HZSM-5(Al) because of the weaker acid strength of HZSM-5(Ga). In addition, phosphorous-modified HZSM-5(Ga) (P/HZSM-5(Ga)) showed good catalytic activity and stability because of the suppression of both carbonaceous deposition and release of gallium from the zeolite framework.

In order to further enhance the catalytic performance of P/HZSM-5(Ga), we have prepared several lanthanum- and phosphorous-co-modified HZSM-5(Ga) zeolites with various La/Ga and P/Ga ratios (La/P/HZSM-5(Ga)) and their ethanol conversion efficiency is evaluated herein. It is well known that doping of HZSM-5(Al) with lanthanum is very effective for the improvement of hydrothermal stability as well as catalytic performance [10,15,19].

2. Experimental

2.1. Synthesis of isomorphously framework-substituted ZSM-5 type zeolite with gallium (HZSM-5(Ga))

Protonated ZSM-5(Ga) (HZSM-5(Ga)) having a SiO_2/Ga_2O_3 ratio of 70 was synthesized by adding gallium nitrate ($Ga(NO_3)_3 \cdot 6H_2O$, Soekawa Chemical Ind. Co. Ltd., Japan), colloidal

* Corresponding author. Tel.: +81 82 424 7607; fax: +81 82 424 5494.
E-mail address: tsano@hiroshima-u.ac.jp (T. Sano).

0926-860X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2011.12.034