# Catalytic activity of ZSM-11 zeolites modified with metal cations for the ethane conversion

Oscar A. Anunziata*, Griselda A. Eimer and Liliana B. Pierella

*CITeQ (Centro de Investigación y Tecnología Química), Facultad Córdoba, Universidad Tecnológica Nacional, CC36 Suc16(5016), Córdoba, Argentina*
E-mail: oanunziata@scdt.frc.utn.edu.ar

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ZSM-11 zeolite samples differing by their active sites ($H^+$ and different metal cations) have been studied in the transformation of ethane into aromatic hydrocarbons. A relationship between Lewis sites increasing–aromatization capacity and possible reaction steps have been suggested.

**KEY WORDS:** ethane conversion; aromatic hydrocarbons; active sites; modified zeolites

## 1. Introduction

Ethane ($C_2$) is a component of a variety of refinery gases. Natural gas (NG) may contain $C_2$ from traces up to more than 10%. According to thermodynamic data, transformation of $C_2$ requires higher temperatures whereas aromatization of propane ($C_3$) and higher alkanes can be carried out at lower temperatures than 500 °C. Thus, the activation of ethane results in an intriguing subject. Pentasil zeolites loaded with metal cations, such as gallium and zinc have been successfully used for activation and conversion of light alkanes into aromatic hydrocarbons (AH). Ono *et al.* [1] studied the $C_2$ transformation indicating that incorporating gallium or zinc into ZSM-5 greatly enhances the activation of ethane and is essential for the formation of aromatics from $C_2$. Solymosi *et al.* [2] reported excellent $C_2$ conversion levels, about 75%, on $MoO_3$/ZSM-5 catalyst into benzene, at the high reaction temperature of 700 °C. Choudhary *et al.* [3] studied direct aromatization of NG over gallium-zeolites, reporting conversion of $C_{2+}$ hydrocarbons in 70% at 600 °C. In our previous papers, we have reported that Zn-ZSM-11 and Mo-ZSM-11 show an excellent catalytic behavior for aromatization of NG and light paraffins [4–8]. Here, we describe $C_2$ transformation over ZSM-11 zeolites modified with different metal cations and suggest possible reaction steps with special emphasis on the relationship between the nature of the active site and the mode of $C_2$ activation.

## 2. Experimental

ZSM-11 zeolites (Si/Al = 17) were synthesized by hydrothermal crystallization in $Na_2O$–$Al_2O_3$–$SiO_2$ systems, in the presence of tetrabutylammonium hydroxide as template [7]. Zn-ZSM-11(20), Zn-ZSM-11(50) and Zn-ZSM-11(80), that presented 20, 50 and 80% ionic exchange percentages, respectively, were prepared by ion exchange of $NH_4$-zeolite with 0.05 M zinc nitrate solution by refluxing. The cations $Pb^{2+}$, $Fe^{3+}$ and $Cu^{2+}$ were incorporated to Zn-ZSM-11(50) by ion exchange, reaching a total ionic exchange percentage of 80%. Mo-ZSM-11 was prepared by impregnating $NH_4$-zeolite with aqueous ammonium heptamolybdate solutions to yield a 2 wt% of Mo, whereas Mo–Zn-ZSM-11 was prepared by impregnating Zn-ZSM-11(50) with aqueous ammonium heptamolybdate solutions to yield a 1 wt% of Mo. Finally, the samples were dried at 110 °C and calcined at 500 °C overnight. Table 1 lists the chemical composition and total surface area obtained by BET of the catalytic materials used in this work. All the catalysts showed high levels of purity and crystallinity obtained by XRD. Infrared measurements were performed on a Jasco 5300 FT-IR spectrometer. The samples were pressed into self-supporting wafers (8–10 mg/cm$^2$) and pyridine (3 Torr) was adsorbed at room temperature and desorbed at 400 °C and $10^{-4}$ Torr. IR data for chemisorbed pyridine interacting with Brønsted acid sites and Lewis sites in zeolite allowed us to determine the concentration of Brønsted and Lewis

Table 1
Chemical composition and total surface area of the catalytic materials used in this work.

| Catalyst | Cation (mol/cell unit) | Cation (wt%) | Surface area (m$^2$/g) |
|---|---|---|---|
| H-ZSM-11 | – | – | 379 |
| Zn-ZSM-11(20) | Zn 0.54 | 0.6 | 356 |
| Zn-ZSM-11(50) | Zn 1.33 | 1.5 | 348 |
| Zn–Pb-ZSM-11 | Zn 1.33, Pb 0.8 | Zn 1.5, Pb 2.8 | 350 |
| Zn–Mo-ZSM-11 | Zn 1.33, Mo 0.61 | Zn 1.5, Mo 1 | 331 |
| Zn–Cu-ZSM-11 | Zn 1.33, Cu 0.8 | Zn 1.5, Cu 0.87 | 312 |
| Zn–Fe-ZSM-11 | Zn 1.33, Fe 0.53 | Zn 1.5, Fe 0.5 | 319 |
| Zn-ZSM-11(80) | Zn 2.13 | Zn 2.4 | 347 |
| Mo-ZSM-11 | Mo 1.22 | Mo 2 | 335 |

* To whom correspondence should be addressed.

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