



# Influence of the parent zeolite structure on chromium speciation and catalytic properties of Cr-zeolite catalysts in the ethylene ammoxidation

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## ABSTRACT

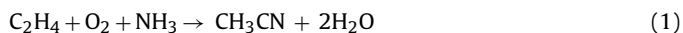
Cr-zeolites with MFI, BEA, MOR and FAU structures, prepared by solid-state ion exchange, were characterized and tested in C<sub>2</sub>H<sub>4</sub> ammoxidation to acetonitrile in the temperature range 425–500 °C. Based on characterization results, chromate and/or polychromate species, oxo-cations and small Cr<sub>2</sub>O<sub>3</sub> oxide clusters played a key role in the ammoxidation of ethylene, while agglomerated Cr<sub>2</sub>O<sub>3</sub> and bare Cr cations should be avoided. Cr ions sited in the sodalite and hexagonal cages of NH<sub>4</sub><sup>+</sup>-Y are not accessible to the reactants while available catalytic sites are poorly active. However, the mesopores of the ultra stable Y zeolite (USY) favor the diffusion of reactants to the clustered Cr oxide. The corresponding catalyst is therefore active, but the presence of octahedral Al species is crucial to the ammoxidation. Cr ions in zeolites beta and mordenite led to less active catalysts when compared to ZSM-5. In zeolite beta, the micropores are small; therefore, pronounced interactions between ethylamine intermediate molecules could discourage the acetonitrile formation. In mordenite, agglomerates of Cr<sub>2</sub>O<sub>3</sub> oxide inhibited the accessibility of active sites to the reactants and enhanced the hydrocarbon oxidation. The catalytic performance of Cr ions in ZSM-5 provided from a synergy of different parameters: structural, textural and the acid strength (Si/Al ratio).

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## 1. Introduction

Acetonitrile is used as a basic feedstock in a wide range of industrial applications [1]. The demand for acetonitrile remains strong, and consequently, various chemical processes were widely used to meet the demand [2]. Unfortunately, most of these conventional processes are hazardous, expensive and less-selective [2].

As an alternative, academic and patent literature has provided much information on the important aspects of light hydrocarbons ammoxidation to acetonitrile. For the direct ammoxidation of ethylene (Eq. (1)), a large number of catalytic systems have been developed using either microporous materials (zeolites) or transition metal oxides as supports.



Li and Armor [3,4], Mies et al. [5,6] and Mhamdi et al. [7–10] reported substantially higher activity of Co/zeolites catalysts with BEA and MFI topologies in ammoxidation of ethylene.

In our preliminary study [11] performed using sol-gel derived materials, aerogel Cr/Al<sub>2</sub>O<sub>3</sub> and Co/Al<sub>2</sub>O<sub>3</sub> catalysts (5 wt.% of metal) were not found to be highly active in ammoxidation of ethylene to acetonitrile. More recently, we reported that Cr-ZSM-5 catalysts (5 wt.% of Cr, Si/Al = 15 and 26) yielded mostly acetonitrile after varying the source of chromium [12] and the catalysts preparation method [13]. Consequently, we concluded that zeolites with Cr ions in the exchange sites seem to be the materials exhibiting higher activity, whereas, agglomerated Cr<sub>2</sub>O<sub>3</sub> oxide enhances the hydrocarbon combustion.

The nature of catalyst support is a crucial parameter which can affect the catalytic properties of Cr exchanged zeolites. Five zeolite supports of MFI, BEA, MOR and FAU structures were provided in this work. ZSM-5 [14] has a three-dimensional intersecting channel system. A straight channel of 0.56 nm × 0.53 nm runs parallel to the *a*-axis and a sinusoidal channel of 0.55 nm × 0.51 nm runs parallel to the *b*-axis (see Table 1 for axis). Zeolite beta [14] has a three-dimensional intersecting channel system. Two mutually perpendicular straight channels run in the *a*- and *b*-directions, each with a cross section of 0.66 nm × 0.67 nm. A sinusoidal channel of 0.56 nm × 0.56 nm runs parallel to the *c*-direction. Mordenite [14] has a semi-two-dimensional

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