



## Ammonoxidation of ethylene over low and over-exchanged Cr–ZSM-5 catalysts

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### ABSTRACT

Catalytic performances of Cr–ZSM-5 catalysts (5 wt.% of Cr, Si/Al = 26), prepared by solid-state reaction and aqueous exchange, from Cr nitrate and Cr acetate precursors, were evaluated in the selective ammonoxidation of ethylene into acetonitrile in the temperature range 425–500 °C. Catalysts were characterized by chemical and thermal analysis, XRD, N<sub>2</sub> physisorption, <sup>27</sup>Al MAS NMR, TEM, UV–vis DRS, Raman, DRIFTS and H<sub>2</sub>-TPR. Characterization results shown that solid-state exchange was favorable for Cr<sub>2</sub>O<sub>3</sub> formation, while exchanging chromium in aqueous phase led, essentially, to Cr(VI) species. Catalysts were active and selective in the studied reaction, and among them, those, prepared from aqueous exchange, exhibited the highest acetonitrile yields (23 ± 0.5%, at 500 °C). Improved catalytic properties can be correlated with the chromium species nature. In fact, mono/di-chromates and/or polychromate species, sited in the charge compensation positions, were definitively shown, as being, the active sites. Furthermore, during solid-state reaction, the agglomeration of Cr<sub>2</sub>O<sub>3</sub> oxide should be avoided since these species inhibit the catalyst activity.

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### 1. Introduction

In the past few decades, a large number of catalytic systems have been developed in our laboratory for light hydrocarbons ammonoxidation into acetonitrile. In fact, numerous works have dealt with the shape-selective ammonoxidation of ethylene using either microporous materials (zeolites) or transition metal oxides as catalyst supports.

For example, the catalytic performance of Co/ZSM-5 catalysts [1–4] has been evaluated in the ammonoxidation of ethylene into acetonitrile. Sol–gel derived Co/Al<sub>2</sub>O<sub>3</sub> and Cr/Al<sub>2</sub>O<sub>3</sub> catalysts have also been used [5].

More recently, we have reported the performance of Cr–ZSM-5 catalysts, issued from solid-state exchange, in the ammonoxidation of ethylene after varying the source of chromium [6]. The selectivity and the yield of acetonitrile largely depended on the nature of the applied catalysts. For example, 26% of C<sub>2</sub>H<sub>4</sub> conversion and 95% of selectivity toward acetonitrile have been reached at 500 °C after choosing an appropriate chromium precursor.

The catalytic activity of Cr–ZSM-5 catalysts in the ammonoxidation of ethylene lies in the variability of oxidation states of chromium, the degree of polymerization (mono/di-chromates or polychromates, etc.), the aggregation state of oxide species and their crystallographic structure (amorphous or crystalline). Thus, it has been accepted that the improved catalytic activity of Cr–ZSM-5 catalysts is due to the presence of (poly)-chromate species and Cr ions in charge compensation positions, while agglomerated Cr<sub>2</sub>O<sub>3</sub> oxide should be avoided [6].

Cr<sub>2</sub>O<sub>3</sub> oxide species provided essentially from the fact that, during solid-state exchange, a non-negligible fraction of Cr ions does not diffuse inside the zeolite channels but remains on the outer surface of the grain. In this way, an optimization of catalysts preparation method would thus consist in tuning the operating conditions and the nature of chromium salt to ensure the effective diffusion of Cr ions inside the zeolite.

In the case of zeolite based catalysts, fundamental studies [7–9] have provided a strong dependence of the exchange level, i.e. the preparation method, and the metal speciation in a wide range of catalytic reactions.

The aim of this work is the comparison between the catalytic behaviors of under- and over-exchanged Cr–ZSM-5 catalysts in the ammonoxidation of ethylene into acetonitrile. It should be underlined that a large part of the work has been devoted to the physicochemical properties of the prepared materials.

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