



Effect of extra-framework Al formed by successive steaming and acid leaching of zeolite MCM-22 on its structure and catalytic performance

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ABSTRACT

Dealuminated MCM-22 samples have been prepared by a two-step dealumination procedure. Detailed assessment of the properties of the materials obtained at each one of the successive stages, i.e. steaming (at 500 °C, 700 °C and 800 °C) and acid reflux (HCl and oxalic), has been made by XRD, N₂ adsorption–desorption, *m*-xylene adsorption, ²⁷Al MAS NMR and FT-IR of pyridine adsorption. It was found that steaming generates extra-framework aluminum (EFAl) species and the majority of them cannot be extracted by the consecutive acid leaching. These extra-lattice entities block the zeolite micropores which makes the remaining Brønsted acid sites isolated and inefficient. It is shown that the presence of such species vastly affects the catalytic performance of zeolite MCM-22 in the reaction of *m*-xylene conversion. The consequences are reduced adsorption capacity and catalytic activity, modified reaction products distribution, enhanced *p*-xylene selectivity, as well as altered mode of coke formation and composition of the coke precursors.

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1. Introduction

Dealumination of zeolite has been studied for several decades but recently the interest towards this modification method has been renewed as one of the several top down approaches for mesopore formation and creation of enhanced Brønsted acid sites, both crucial factors in determining the activity and selectivity in the transformations of aromatic hydrocarbons on zeolite catalysts [1]. Among the typical examples for such procedure, giving rise to a very significant catalyst improvement, are the well-known ultra-stable Y (USY) family materials featuring mesopores [2] which are obtained by dealumination via steam treatments and are being widely used in the petrochemical industry. The effectiveness of dealumination by steaming and/or acid leaching depends on both the severity of the procedure and the zeolite structure. During this treatment extra-framework aluminum species (EFAl) are generally formed, which could be removed from the lattice, and secondary mesoporosity might be created [3]. The non-framework aluminum generated by hydrothermal treatment can be easily extracted by the subsequent acid leaching but only in case of three-dimensional, large-pore zeolites [4,5]. Dealumination of more siliceous zeolites,

such as ZSM-5 or other structures induces rather limited mesoporosity [6–8].

The literature survey reveals that oxalic acid extracts the aluminum expelled upon previous hydrothermal treatment only from large-pore but not from medium-pore zeolites because of diffusion limitations [9,10]. Mordenite is suggested to imply diffusion problems too in removing, by mineral acid treatment, the EFAl from its one-dimensional pore structure [11]. It is observed by Fernandes et al. [12] that not only in mordenite but also for zeolite beta, steam dealumination generates highly polymerized EFAl which can be partially removed by the subsequent acid leaching.

The particular structure of the zeolite MCM-22 holds out interesting opportunities for studying the process of dealumination and the consequences of this procedure for its catalytic performance [13]. This zeolite is composed of two channel systems, both of them accessible through narrow 10-MR windows [14]. The material contains at least five crystallographically non-equivalent T-sites and they are affected to different extents by the mineral acid dealumination [13]. Partial dealumination takes place still during the calcination of this lamellar structure [15]. Dealumination is more severe on heating in air than in vacuum or N₂, and may occur even during grinding in a mortar [16].

Studies on hydrothermally dealuminated MCM-22 zeolites show that aluminum released from the lattice mainly stays in the internal pore systems and then condenses into polymeric aluminum species, which causes a decrease in the accessibility of the

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