Zeolites are widely used heterogeneous catalysts in the field of chemistry and refining. These microporous and crystalline aluminosilicates exhibit a strong Brønsted acidity making them attractive for processes such as hydrocracking and fluid catalytic cracking. However, micropores can induce diffusion limitations and confinement effects resulting in the formation of undesired side products. Posterior introduced mesopores, leading to the so called “hierarchical zeolites” can overcome these phenomena. They contain bi- or multimodal pore structures which can be post-synthetically introduced by partial dealumination and/or desilication of the framework. In the last years these hierarchical zeolites became of great interest for the scientific community. Synthesis procedures and their consequences on the properties of zeolites were optimized in a great extent at a mesoscale. However, at a molecular scale the mechanisms of this mesopore formation and their impact on the nature of the resulting active sites were much less debated in the literature. In the present review, we focus on state-of-the-art knowledge of these aspects at the molecular scale. Spectroscopy techniques (such as NMR, FTIR, XAS), microscopy and density functional theory approaches, dealing with the mechanism of Si/Al removal and nature of the resulting extraframework species are gathered and discussed. This analysis of the literature reveals that the atomic scale’s understanding of the mesopore formation during desilication and dealumination remains a current scientific challenge.

ABSTRACT

Keywords:
Hierarchical zeolites
Dealumination
Desilication
Atomic scale

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1. Introduction

Nowadays solid acid catalysts have a widespread application field for example in refining, petrochemistry [1], environmental protection [2,3], medicine [4,5] for the synthesis of bio-fuels and bio-chemicals [6,7] and in the field of adsorption [8], inter alia. Among these catalysts, zeolites which are crystalline aluminosilicate microporous materials, have drawn a strong attention since their first use as adsorbents for industrial separation and purification which is mainly due to their intrinsic and post-synthetic characteristics. Their strong acidity, among others resulting from Lewis- and Brønsted-acid sites, linked with their thermal robustness and well manageable pore sizes make them suitable candidates for industry reactions such as fluid catalytic cracking, hydrocracking, isomerisation and alkylation of various hydrocarbon molecules [9]. Historically, the first synthetically made zeolite appeared in the late 1940s [10] and the introduction in hydrocracking may be directly influenced by confinement effects [11]. The major topic in zeolite synthesis lies 20 years later revolutionized the field of application of these porous materials [11]. The major topic in zeolite synthesis lies within the tailoring of the shape size and the connectivity of intra-framework channels. However confinement effects [12] and diffusion limitations impose severe constraints on the reactants, intermediates and products. For instance, the selectivity in hydrocracking may be directly influenced by confinement effects [13].

One solution is the use of ordered mesostructured solids such as MCM-41 (Mobil Composition of Matter–41), one of the most known ordered mesoporous silica, developed in the early 1990’s by Mobil Oil Company (now Exxon Mobi). Contrasting with zeolites, these materials have larger pores and well manageable pore size distributions [14–16]. MCM-41 displays an hexagonal arrangement of mesopores of around 2–6.5 nm [17,18] and for their synthesis supramolecular ionic surfactants, e.g. alkyltrimethylammonium halides, called structure directing agents (SDA) are used. Since the mesoporous siliceous structures do not exhibit the desired Brønsted acid site, they need to be subjected to postsynthetic functionalisations, so called “grafting” [19] with aluminium isopropoxide in n-hexane [20] for example. However, the acidity of aluminium-doped MCM-41 is globally closer to amorphous silica–alumina [21]. Additionally, since these materials are thermically and hydrothermically less stable [14] (Al is easily removable from the framework) than zeolites, they are less suitable in processes such as fluid catalytic cracking or hydrocracking.

With that respect, “hierarchical zeolites” [22] have opened new perspectives because they show improved catalytic performances compared to non-treated ones, e.g. for Mordenite, Zeolite Y and ZSM-5 [23]. There are two possibilities leading to these hierarchical zeolites: either the template or the non-template method [22,24]. Where the first one lies in an ab initio tailoring of the shape size and connectivity within a zeolite by bulky templating agents during crystallization [25], the second method uses already synthesized zeolites followed by dealumination [26–28] and/or desilication [29–32] to create intracrystalline mesopores. The dealumination is performed by steaming and/or acid leaching [33,34]. Although thermal treatment is sufficient to create local defects in zeolites, steaming combined with acid leaching is preferred in most cases since it makes the Si and Al debris more labile (extraframework species–extraframework aluminium EFAL and silicon EFSI – and amorphous silica–alumina) within the pores enhancing the diffusion properties of the catalysts. The second demetallation (desilication) consists in selectively removing the silicon from the framework by dint of aqueous basic conditions [35–37].

One remaining delicate problem is the characterization of extraframework species [38–42] within the cavities and the newly formed mesopores as well as the nature of the resulting acid sites. To elucidate this problem one has to understand the mechanism of formation of such extraframework species and their mobility taking place during the dealumination and desilication steps as well as the accurate description of both crystalline and local amorphous phases. Several reviews already focused on the synthesis of aluminium-containing mesostructural materials [43], the generation, characterization and impact of mesopores in zeolites [44,45], and the enhanced utilization of hierarchical zeolites in catalysis [22,46]. Despite significant achievements in the control of synthetic procedures and the mesoscale knowledge of the porous structure after demetallation, the previous reviews did not address the nanometric – even molecular – scale’s origins of the demetalation mechanisms, and of the improved performances of the resulting solids. Consistently, the present review article aims at analyzing published works attempting to elucidate the possible atomistic scale mechanisms for the dealumination and desilication by dint of experimental techniques and emerging computational chemistry methods. The impact on the resulting properties of zeolites must rather be viewed as a highlight into non-exhaustive examples.

In the present review, Mordenite, Faujasite and ZSM-5 (Fig. 1) were chosen as model systems due to their large application field mainly in oil refinery (e.g. Fluid catalytic cracking and Hydrocracking) and their large application field as shape-selective compounds catalyzing reactions such as isomerisation, alkylation and cracking. Hence, Section 2 will focus on these post-synthetic modified zeolites from the point of view of synthesis and resulting features known at a molecular scale. We will address the dealumination/desilication processes and the formed species under given treatment conditions. Then, mechanistic approaches on the dealumination/desilication reactions available from both experimental and theoretical data will be presented in Section 3. Some challenges open for future studies will then be suggested.

Note that, although the recent outcomes of zeolite demetallation has shown, that a combination of dealumination and desilication paths is the key to obtain inter alia well manageable pore sizes as well as enhanced catalytic characteristics compared to non-treated zeolites [32], we treat the two pathways separately. This is due to the fact that we focus on the mechanistic approaches of the dealumination and desilication at the molecular scale. At this scale, each step has to be decoupled, and studied independently, or consecutively (to mimic the synthetic procedure). In particular, at the single scale, one would like to better understand which Al–O and/or Si–O bonds are formed or broken for each relevant step. So we chose to present dealumination and desilication separately.