Zeolites as Catalyst Supports for Hydrocarbon Oxidation Reactions

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Catalytic oxidation is a key technology for the conversion of petroleum-based feedstocks into useful chemicals (e.g., adipic acid, caprolactam, glycols, acrylates, and vinyl acetate) since this chemical transformation is always involved in synthesis processes. Zeolites are microporous, crystalline aluminosilicate materials known since 1756 when the stilbite structure was identified by the Swedish mineralogist Crönstedt. Zeolites and other related porous materials can be supports for organometallic or metallic active species. These materials are the most studied supports due to their combined properties of mechanical and thermal stability that allows it an easy regeneration and recycling.

hydrocarbon oxidation reactions   zeolites   hierarchical zeolites   immobilized catalyst

1. Industrial Hydrocarbon Oxidation Reactions

Catalytic oxidation reactions are of high industrial relevance since many important commodities have synthesis paths involving oxidation. To understand their relevance, it can just refer to adipic acid, with a global production of over 4 million tons and expect to exceed a \$8 billion USD global market by 2025 [1].

When addressing hydrocarbon oxidation reactions, there are several significant industrial applications. The direct oxidation of alkanes is an attractive alternative to oxidation via olefins; however, only two industrial processes have been implemented, and other alkanes oxidations are only at the research or pilot plant status. One of these reactions is the production of maleic anhydride from *n*-butane (**Figure 1**).
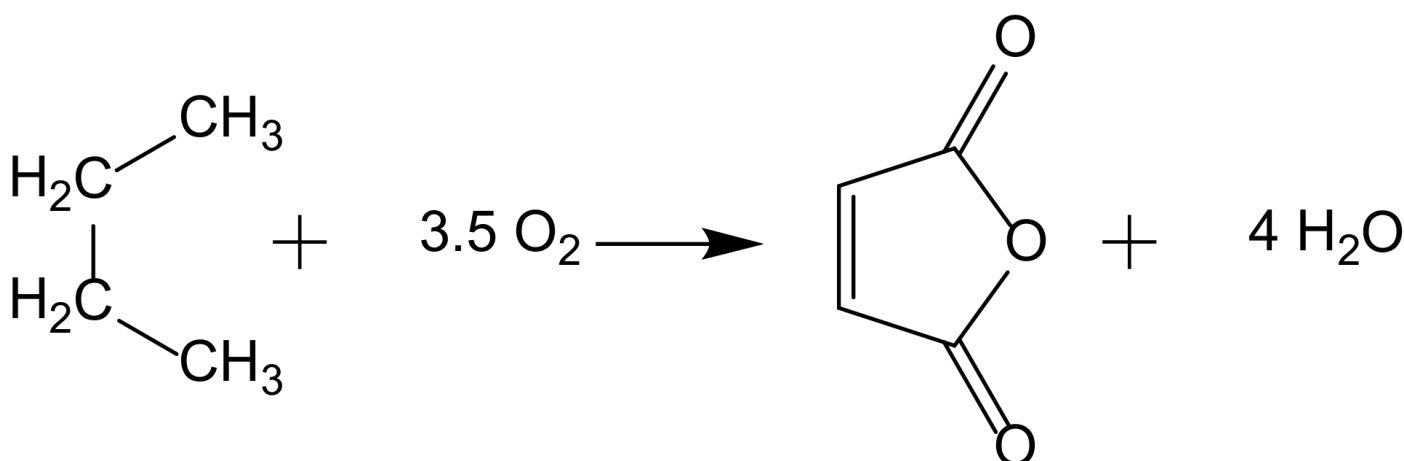
Figure 1. Maleic anhydride synthesis from *n*-butane oxidation.

This process uses supported $(VO)_2P_2O_7$ as heterogenous catalyst and achieves high weight yields (ca. 95%) replacing a previous method with benzene. In both methods, butane (or benzene) is fed into a stream of hot air, and the mixture passes through a catalyst bed at high temperature. Fixed, fluidized, and transport bed reactors technologies have been implemented in different industrial plants to address different technical difficulties [2].

Another example of alkane oxidation but in the liquid phase with homogeneous catalysis is the oxidation of cyclohexane into a mixture of cyclohexanol and cyclohexanone (also known as KA oil), which are intermediates in the manufacture of nylon-6 and nylon-6,6. KA oil is mainly obtained through the oxidation of cyclohexane using air or peroxide as the oxidant agent. In the present industrial conditions, liquid phase oxidation of cyclohexane is achieved at about 165 °C and O_2 pressures of 8–15 bar in the presence of manganese or cobalt naphthenates as catalysts (**Figure 2**). To avoid oxidative side reactions, a short retention time is used to assure 80–85% selectivity; thus, the conversion is limited to 10–11% per cycle, requiring separation and refeeding of the unconverted cyclohexane. Additionally, the currently used homogeneous catalysts are difficult to separate from the reaction media, leading to serious environmental pollution. [3]
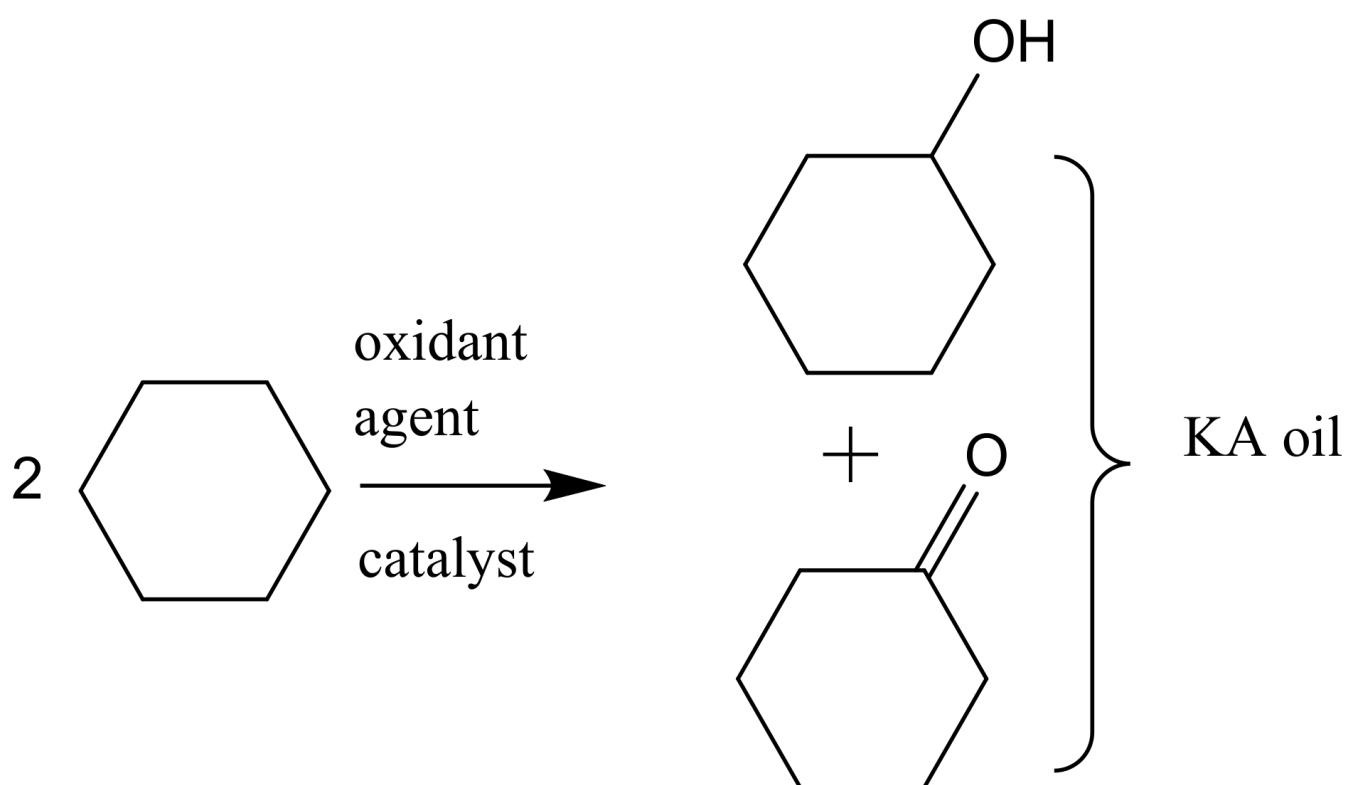
Figure 2. Oxidation of cyclohexane to cyclohexanol and cyclohexanone (KA oil).

There are several industrial alkenes oxidation processes, and two of the major products obtained by these methods are ethylene oxide and acetaldehyde. Both chemicals are produced from ethylene and are in turn raw

materials to produce other compounds such as ethylene glycol, diethylene glycol, triethylene glycol (from ethylene oxide) and acetic acid, acetate esters, and pyridine derivatives (from acetaldehyde).

The current ethylene oxide production process was developed in the middle of the 20th century and uses finely dispersed metallic silver together with alkali and alkaline earth metals promoters, on ultrapure aluminum oxide, i.e., a low surface area support. There are two variations of this process: one uses air and the other oxygen, and both use fixed bed reactors which consist of large bundles of thousand tubes, each with a length of approximately 10 m and an internal diameter of 20–50 mm. The temperature and the pressure range between 200 and 300 °C and 15 and 25 bar, respectively.

The oxidation of ethylene to acetaldehyde, known as the Wacker process, was one of the first industrial homogeneous catalytic process (Scheme 1). The catalyst is a two-component aqueous solution consisting of $PdCl_2$ and $CuCl_2$, and from the proposed mechanism, O_2 is not directly involved.

$$C_2H_4 + PdCl_2 + H_2O \quad \rightarrow \quad CH_3CHO + Pd^0 + 2\ HCl$$

$$Pd^0 + 2\ HCl \quad \rightarrow \quad PdCl_2 + Cu_2Cl_2$$

$$Cu_2Cl_2 + 2\ HCl + \tfrac{1}{2}\ O_2 \quad \rightarrow \quad 2\ CuCl_2 + H_2O$$

$$C_2H_4 + \tfrac{1}{2}\ O_2 \quad \rightarrow \quad CH_3CHO$$

Scheme 1. Proposed mechanism for the ethylene oxidation to acetaldehyde.

The process is a two-phase gas/liquid system, and there are variations in different industrial units, with some using a single-step process and others a two-step process. Each solution has different operational conditions and advantages.

As the final examples of substrates used in industrial hydrocarbon oxidation reactions, it can include the oxidation of aromatic hydrocarbons. Even though benzene oxidation is still not near industrial application, due to increasing ring activation with oxidation and further reactions, other molecules are already used.

The production of phthalic anhydride, a precursor of phthalate esters plasticizers, dyestuffs, and pharmaceuticals, is based on the oxidation reaction of naphthalene. Initially, the process was liquid phase based but was

subsequently replaced by a cleaner gas phase process using mercury salt as a catalyst. A variation of this process uses *o*-xylene instead of naphthalene with further variations in the used catalysts (**Figure 3**).

(a)

(b)
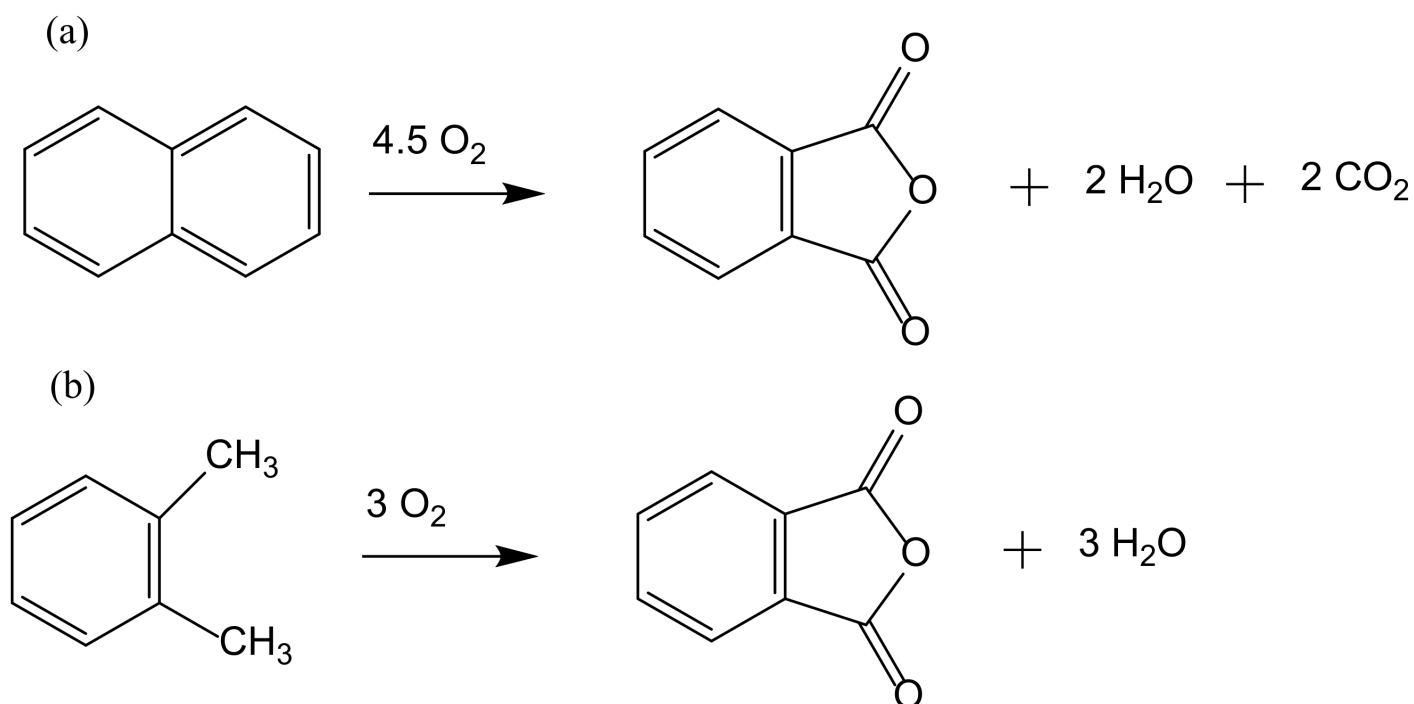
Figure 3. Oxidation of naphthalene (**a**) and *o*-xylene (**b**) to phthalic anhydride.

A xylene isomer is also used in one of the most important industrial oxidation reactions, the production of terephthalic acid from *p*-xylene (**Figure 4**). The relevance of terephthalic acid is based on being the precursor to polyethylene terephthalate (PET), the highest volume synthetic fiber. Since the 1960s, terephthalic acid has been mainly produced by the Amoco process; this homogeneous catalytic process uses soluble cobalt salt (acetate or naphthenate) simultaneously with manganese or bromide ions [4][2].
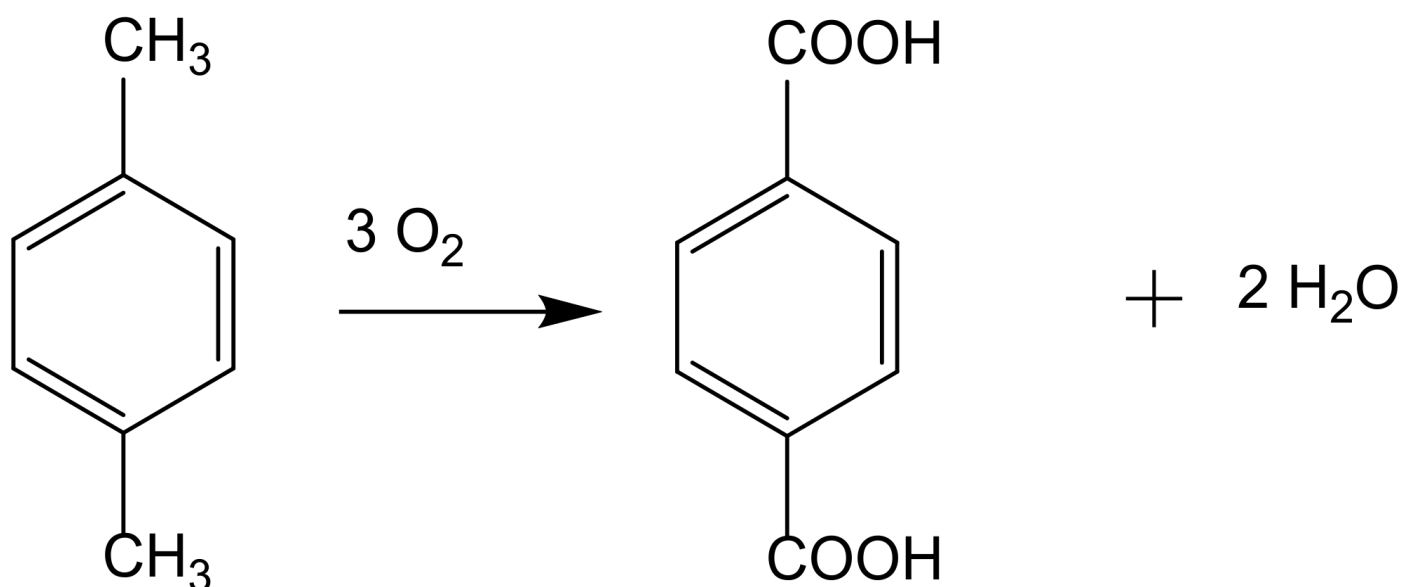
Figure 4. Terephthalic acid production from *p*-xylene oxidation.

2. From Homogeneous to Heterogenized Catalysts

The development of sustainable methods for the catalytic oxidation reactions of hydrocarbons-alkanes, alkenes, and aromatics is an important scientific challenge with significant technological potential. As mentioned previously, these reactions usually occur in the presence of traditional homogeneous catalysts, such as transition and neat metals or their salts, as well as mineral acids and complexes, due to their high activity and selectivity to the desired products. However, the intensive use of these catalysts is rather controversial due to the difficult separation and recovery of the catalyst from the reaction media. The immobilization of catalytic active species in solid supports is a possible strategy to overcome some of the disadvantages of homogeneous processes. Heterogenized catalysts are easily recovered from the reaction media, without expensive separation processes and large amounts of solvents involved, with the additional advantage of allowing the reuse of the catalyst in several cycles. These are, in fact, the main objectives that one expects to achieve through the immobilization of homogeneous catalysts, but some additional benefits may also be obtained, namely when porous supports are considered. In this case, the confinement effects may enhance the interaction of the substrate with the catalyst. However, the porosity of the support may also impose some diffusional constrains that, especially when voluminous subtracts are considered, can result in an extensive loss of activity. In the case of complexes, the immobilization on solid supports has another additional benefit since it prevents dimerization phenomena that are some of the most common causes of homogeneous catalysts deactivation.

3. Zeolites and Related Materials as Support for the Heterogenization of the Catalysts

Zeolites are microporous, crystalline aluminosilicate materials known since 1756 when the stilbite structure was identified by the Swedish mineralogist Crönstedt. This class of materials is composed of corner-sharing TO_4 tetrahedra, where T represents Si or Al. Adjacent SiO_4 and AlO_4^- tethraedra are bridged by oxygen atoms that are arranged in a regular way, giving a three-dimensional system of cages and pores with dimensions comprised in the microporous range, i.e., between 3 and 20 Å, which is responsible by the "molecular sieving" property [5].
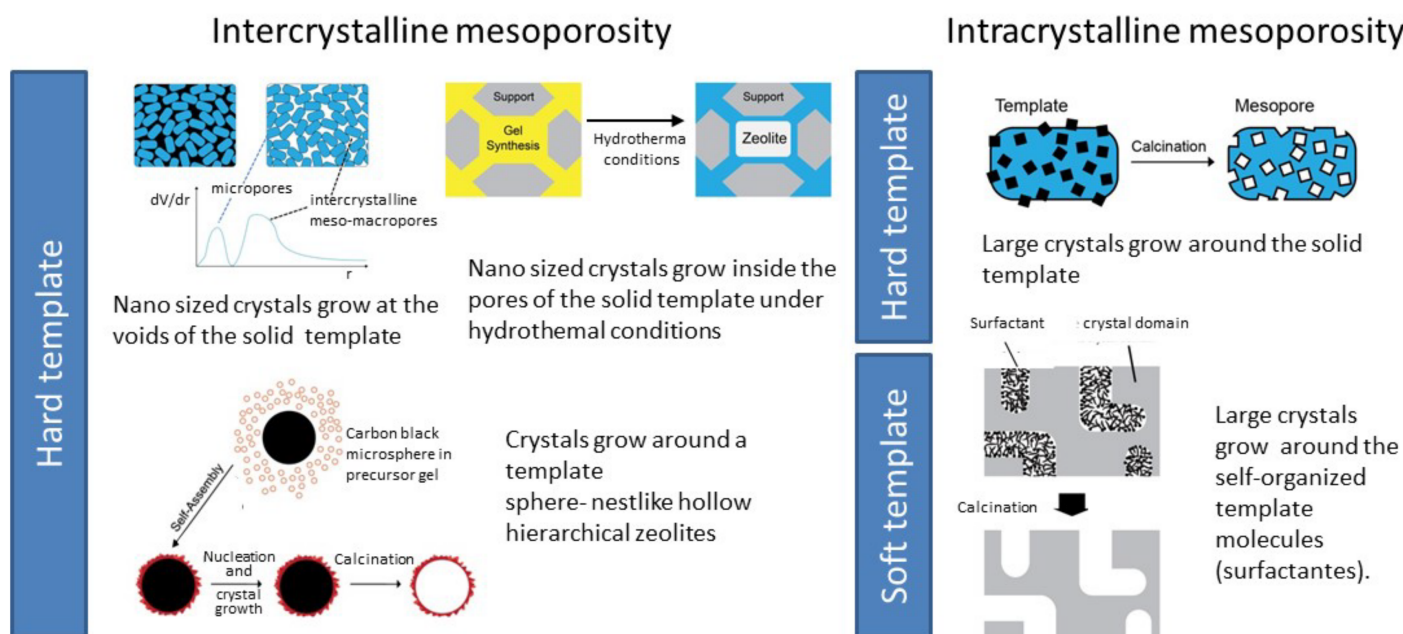
3.1. Hierarchical Zeolites

The strictly microporous nature of zeolite structures is responsible for the various types of shape selectivity that are fundamental to increasing the yield of a desired product. A classic example of shape selectivity is an important petrochemical reaction catalyzed by ZSM-5 zeolite (MFI structure): the transformation of *m*-xylene into *o*-xylene and, especially, *p*-xylene, which is the building block to produce polyethylene (PET)-based products. In this case, opposing the thermodynamic equilibrium where the more stable *m*-xylene is favored, the diffusional limitations for the molecular transport of *m*-xylene and *o*-xylene lead to the conversion of these two more voluminous isomers into the most valuable *p*-xylene [6][7]. Despite the importance of shape selectivity in several reactions catalyzed by zeolites, their native microporosity can also impose diffusion constraints that will limit the catalytic performance,

especially in the presence of bulky molecules. Although a large number of strategies have been proposed and demonstrated, the production of these hierarchical materials can be classified into two major categories: synthesis procedures, also called "bottom-up", or postsynthesis procedures, also called "top-down"[8].

3.1.1. Bottom-Up Strategies

To introduce a supplementary pore system, usually mesopores, several strategies involve the addition of hard or soft templates to the synthesis gel, allowing the crystallization of the zeolites around those templates, giving intracrystalline mesoporosity. Alternatively, the crystal can grow at the confined space between particles, originating small crystals where the mesopores appear as the consequence of the particle stacking (intracrystalline mesoporosity), as schematized in **Figure 5**. In both cases, after synthesis, the templates are removed by combustion, exposing the mesopores.

Figure 5. Overview of the various bottom-up synthesis methodologies to obtain hierarchical zeolites.

3.1.2. Top-Down Strategies

Postsynthesis or top-down strategies comprise the treatments performed on previously synthesized zeolites, aiming to modify its porosity through the creation of a secondary pore system, generally mesopores. Some strategies are low cost since they involve cheap and common reactants to modify the zeolite porosity. On the other hand, the starting materials are generally commercial and robust structures with consolidated properties in adsorption and catalysis fields. The most common strategy to develop mesoporosity in a presynthesized zeolite is the demetallation, i.e., the removal of T atoms, either aluminum (dealumination), or silicon (desilication). Unfortunately, a common drawback of these procedures is that they may lead to significant mass losses that are reflected in significant impact on zeolite crystallinity and acidity. This is particularly important in more sensitive zeolite structures; thus, a careful choice of the experimental conditions, such as temperature, acid/base

concentration, and duration of the treatment, is fundamental for obtaining hierarchical porosity, not disregarding other important properties such as crystallinity and acidity.

3.2. Mesoporous Silicas and Composite Hierarchical Materials

Mesoporous molecular sieves (MMS) are characterized by high surface area (800–1400 m^2 g^{-1}), large pore volumes, and tunable pore dimensions (2–50 nm). The arrival of the first member of the M41S family in 1991, designated as MCM-41 [9], carries great expectations for possible applications of these materials in catalysis and adsorption, overcoming the limitations of zeolites due to their intrinsic microporosity. Later, other related mesoporous silica materials, namely MCM-48, MCM-50, and SBA-15, were synthesized [10]. Recently, more robust mesoporous silica materials have been presented, such as, TUD-1 [11], FDU-12 [12], or KIT-6 [13]. However, despite MMS materials possessing large pores when compared to zeolites, which allows for improving molecular diffusion, and some improvement on the stability having been attained in the last years, their lack of acidity hinders the application of these materials to a wide range of catalytic reactions, when compared with traditional zeolites [10], limiting their use mainly as catalyst supports.

Composite materials are characterized by a mixture between a zeolite, which contributes to its characteristic microporosity, and another material that must be porous itself, or alternatively, contributes to the generation of intercrystalline porosity due to particle stacking. Schwieger et al. [8] reported several combinations of composite materials: the simplest approach is the shaped zeolitic bodies, comprising the mixture of a powder zeolite with a binder material, that, after compacting and shaping operations, originates pellets, beads, cylinder, etc., with interparticle macropores on the packed bed level, when used as reactor/column filling. More technological approaches include coating strategies where a support surface is functionalized with a zeolitic material, originating hierarchically organized materials with two or three levels of porosity. The preparation of these materials can be performed according to two strategies: ex situ coating where a layer of a presynthesized zeolite is deposited on a support such as alumina foams [14] or cordierite monoliths [15] and in situ coating comprising the direct hydrothermal synthesis of a zeolite on a support surface. In this later case, the supports can be classified as inert or reactive: in the first case, the crystallization of the zeolite takes place at the external surface of the support keeping it unchanged [16], but on the other hand, in the presence of reactive supports such as SiO_2 or Al_2O_3, a fraction of the support is consumed with consequent incorporation and intergrowth between the zeolite layer and the residual support material [17][18]. Recently, the combination of a microporous zeolite with a mesoporous material has gained much attention, comprising a core–shell system where the core is made of zeolitic microporous material surrounded by a mesoporous shell. These composite materials combine two organized pore systems: a microporous zeolite containing the active sites enwrapped in a mesoporous material with large transport channels, leading to an improvement on both catalytic and adsorption behavior. Examples of core–shell materials can be found on the literature using several zeolite structures such as MFI [19][20] FAU [21], and MWW [22] enwrapped by mesoporous molecular sieves such as SBA-15 and MCM-41, bringing a new opportunity for the application of these mesoporous molecular sieves.

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