

# Mesoporous materials from zeolite seeds as supports for nickel tungsten sulfide active phases Part 1. Characterization and catalytic properties in hydrocracking reactions

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## Abstract

MCM-41 aluminosilicate mesostructures (Si/Al = 18) with hexagonal long-range order were assembled from protozeolitic nanoclusters (zeolite seeds) that normally nucleate the crystallization of  $\beta$ -zeolite (BEA). Depending on the duration of the thermal treatment leading to the zeolite seeds, different acidic materials can be obtained. For short pre-treatment duration, the material presents the main characteristics of the MCM-41, whereas for longer pre-treatment duration, there is a gradual transition to a mostly zeolitic one. Hydrocracking of *n*-decane was carried out on catalysts composed of a sulfided nickel tungsten phase supported on various  $\beta$ -MCM-41 supports as well as on an amorphous silica–alumina and an AISBA-15 material. The hydrocracking properties of the catalysts are related to the nature of the  $\beta$ -MCM-41 and vary from the comportment of silica–alumina materials to the one of a zeolite. The nickel-tungsten catalyst supported on  $\beta$ -MCM-6 (6 h pre-treatment for the zeolite seeds solution) is more active and more selective toward isomerization than the catalyst supported on a commercial silica–alumina support.

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## 1. Introduction

Hydrocracking is a flexible process for the conversion of heavy, low quality feedstocks into lighter, highly valuable transportation fuels [1,2]. In addition to the cracking of the molecules, the mild hydrocracking process ensures the elimination of sulfur and nitrogen-containing molecules as well as a deep saturation of aromatics. This allows the production of high quality fuels, which will match the future stringent specifications. Hydrocracking catalysts are bifunctional, associating a hydro–dehydrogenating function with an acidic one. Due to the presence of sulfur and nitrogen

impurities, mixed sulfides, such as NiMo or NiW are usually chosen as hydro–dehydrogenating phases. In particular, NiW catalysts will be chosen if the objective of the process is to obtain gasoils fractions with a high cetane number, which implies a severe reduction of the aromatics content, and consequently rather high hydrogenating properties for the catalyst [3,4]. Similarly, the choice of the solid providing the acidic function will depend on the objective of the process. If gasoline is the required product, the acidic component of the catalyst will be preferably a zeolite whereas silica–alumina will be preferred to produce high yield of gas oil. Furthermore, high activity levels can be achieved with zeolites, which is not the case with conventional silica–alumina. The reason of the high activity and cracking selectivity of zeolites is their strong acidity which favours successive cracking reactions, and as a

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consequence, the formation of light products. The main drawback of zeolites utilization is related to their essentially microporous system which prevents the diffusion of bulky molecules present in heavy feedstocks. This is the reason why there has been a continuous interest in finding materials that possess the characteristics of zeolites (strong Brønsted acidity, high surface area, and controlled pore size) but with larger pore sizes. Besides zeolites with large and ultra-large pores, several kinds of materials have been proposed as supports for cracking and hydrocracking reactions, such as Al-MCM-41 [5], delaminated zeolite (ITQ-2) [6], etc.

Recently, important advances toward the synthesis of materials presenting strong acidity in an open porosity have been made through the assembly of nanoclustered precursors that normally nucleate the crystallization of microporous zeolites. This approach was first demonstrated by Liu et al., using faujasite zeolite (FAU) seeds as building blocks for the formation of an ordered hexagonal mesophase [7]. Additional studies successfully assembled strongly acidic MCM-41 using ZSM-5 (MFI) and Beta (BEA) zeolite seeds as precursors [8–12]. In a previous paper [13], the fine characterization of materials prepared by the organization of BEA zeolite seeds led us to the conclusion that the duration of the hydrothermal treatment leading to the formation of the zeolite seeds solution ( $t_{\text{seeds}}$ ) is a key parameter to adjust the properties of the final material. Indeed the cracking activity increases gradually with  $t_{\text{seeds}}$ , even if no XRD line of the BEA structure and no microporosity are observed up to duration of 16 h (Si/Al = 30). The characterization of the acidity of the sample obtained after a duration of 10 h shows the presence of strong Brønsted sites usually observed in zeolite ( $\Delta\nu(\text{OH}) = 310 \text{ cm}^{-1}$ ,  $\Delta\nu(\text{CO}) = 34 \text{ cm}^{-1}$ ). Consequently, it appeared interesting to us to utilize these new materials as support (denoted  $\beta$ -MCM-41) for a nickel tungsten sulfide phase and to examine their catalytic properties for hydrotreating reactions. We report in this paper a preliminary work on this subject. The model reaction used was the hydrocracking of *n*-decane, under conditions similar to the industrial ones: fixed-bed dynamic reactor, high hydrogen pressure and extrudates obtained by mixing the  $\beta$ -MCM-41 materials with alumina in appropriate proportion. The activities and selectivities of these NiW/ $\beta$ -MCM-41 catalysts were compared to those of catalysts with the same active phase but supported on Al-SBA-15 and a more conventional hydrocracking–hydroisomerization support: an amorphous silica alumina (ASA).

## 2. Experimental

### 2.1. Preparation of $\beta$ -MCM-41

The preparation procedure involves two steps. In the first step, a BEA precursor solution with a molar composition of  $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{Na}_2\text{O}:\text{TEAOH}:\text{HCl}:\text{H}_2\text{O} = 1:0.03:0.028:0.60:0.2:20$  was prepared. The synthesis was adapted from the

literature [11]. Typically, 50.0 g of fumed silica were dissolved in a mixture-containing 267.5 g of a 27 wt% tetraethylammonium hydroxide (TEAOH) aqueous solution, 3.7 g of  $\text{NaAlO}_2$ , 47 ml HCl (3.7 M) and 62.0 g of distilled water. After stirring for 4 h, the opalescent gel was transferred into an autoclave (volume 100 ml) and heated at 413 K for a given time noted  $t_{\text{seed}}$  included between 6 and 16 h. The hydrothermal treatment was stopped by cooling the autoclave with water. The zeolite seeds solution was obtained.

In the second step, typical synthesis of mesoporous material was carried out as follows: (1) 125 g of CTAB was dissolved in  $\text{H}_2\text{O}$  to form 500 g solution under stirring. (2) The obtained zeolite seeds solution was poured into 240 g surfactant solution prepared above, followed by the addition of 40 ml HCl (3.7 M). (3) The white mixture was further stirred for 1 h and loaded into autoclaves for crystallization at 413 K for 36 h.

The final product was recovered by filtration, ion-exchanged three times with 1.0 M  $\text{NH}_4\text{Cl}$  at 353 K each time for 1 h, washed with water and calcined at 823 K for 4 h.

The different supports are named  $\beta$ -MCM-6,  $\beta$ -MCM-10 and  $\beta$ -MCM-16 according to the  $t_{\text{seeds}}$  time in hour. Their Si/Al ratio is equal to 18.

### 2.2. Preparation of the extrudates

Extrudates, analogue to those used in industrial applications were prepared by mixing the  $\beta$ -MCM-41 materials and alumina (commercial product of Condea,  $240 \text{ m}^2 \text{ g}^{-1}$ ) in appropriate proportions according to weight. For example, 15%  $\beta$ -MCM denotes the support containing 15% of  $\beta$ -MCM-41 material and 85% alumina. De-ionized water was added to  $\beta$ -MCM-41 and alumina powders to prepare the dough. This dough was then passed through a stainless steel extruder equipped with a dice with orifices of 8 mm in diameter. The drawn extrudates were then left at room temperature for a few hours and dried in an oven at 393 K overnight. The dried extrudates were finally calcined at 823 K for 4 h.

### 2.3. Reference catalysts

An Al-SBA-15 (Si/Al = 17.2) mesoporous materials and an amorphous silica–alumina from Grace Cooperation (Si/Al = 5.7) were taken as references. The Al-SBA-15 material was prepared by post-synthesis alumination of a pure silica SBA-15 [14] with an aluminum chlorhydrate (ACH) solution, as described by Mokaya for the preparation of Al-MCM-41 [15]. The detailed preparation procedure is given in [16]. The extrudates of all these supports were without alumina addition. For sake of clarity, they will be denoted 100% AISBA and 100% ASA.

### 2.4. Preparation of NiW catalysts

NiW supported catalysts were prepared by incipient wetness co-impregnation using salt solutions-containing appropriate concentrations of  $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_6\text{H}_2$

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