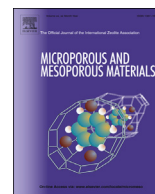




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# Microporous and Mesoporous Materials

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## Synthesis of mesoporous zeolite catalysts by *in situ* formation of carbon template over nickel nanoparticles



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### ABSTRACT

A novel synthesis procedure for the preparation of the hierarchical zeolite materials with MFI structure based on the carbon templating method with *in situ* generated carbon template is presented in this study. Through chemical vapour deposition of coke on nickel nanoparticles supported on silica oxide, a carbon-silica composite is obtained and exploited as a combined carbon template/silica source for zeolite synthesis. This approach has several advantages in comparison with conventional carbon templating methods, where relatively complicated preparative strategies involving multistep impregnation procedures and rather expensive chemicals are used. Removal of the carbon template by combustion results in zeolite single crystals with intracrystalline pore volumes between 0.28 and 0.48 cm<sup>3</sup>/g. The prepared zeolites are characterized by XRD, SEM, TEM and physisorption analysis. The isomerization and cracking of *n*-octane is chosen as a model test reaction and the mesoporous zeolite catalyst is found to exhibit higher activity than the conventional catalyst.

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### 1. Introduction

Zeolites represent the most important group of industrial catalysts offering a wide range of applications from oil refining, petrochemistry and the synthesis of fine chemicals to environmental catalysis [1–4]. Zeolites are crystalline microporous materials that possess a well-defined structure with pore sizes in the range of molecular dimensions as well as strong acid sites. This makes zeolites unique catalysts that can provide excellent size- and shape-selectivity. Moreover, their tuneable chemical composition, high surface area and large pore volume along with high thermal, hydrothermal and mechanical stability make zeolites very attractive heterogeneous catalysts [5,6] and support materials that can incorporate metal nanoparticles or nanoclusters inside the micropore cavities [7–9]. Furthermore, zeolites modified with metal nanoparticles may combine the attractive properties of zeolites with the special catalytic properties of metal nanoparticles to give novel bifunctional catalytic materials where synergistic effects are exploited [10–12].

Unfortunately, zeolites often suffer from severe diffusion limitations that in some cases may induce a negative impact on the catalytic performance of zeolite catalysts. This is related to the intracrystalline transport of the reactants and products to and from the active sites in the zeolites, especially in the reactions that involve large and bulky compounds. Additionally, in some reactions, coke formation enhances these limitations, as the coke deposits block the zeolite micropores, causing a rapid decrease in the catalytic activity [13,14]. Therefore, large efforts have been made in order to improve the catalyst performance. This has been realized by reduction of the intracrystalline diffusion path length in the following possible approaches: synthesis of zeolites with extra-large pores [15–20], direct synthesis of zeolite nanocrystals [21–27], by exfoliating layered zeolites [28,29], and by introducing mesopores in the microporous materials through templating strategies [14,30,31] or demetallation processes [4,32–36].

Over the last years hard-templating strategies for the preparation of hierarchical zeolites and particularly the carbon templating method for the preparation of mesoporous materials have attracted considerable attention [14,30,37,38]. The creation of mesoporosity is beneficial for catalytic applications as it facilitates efficient mass transport of reactants and products in the mesopores [33]. Additionally, mesoporosity in zeolites leads to a better dispersion of

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active metal particles to maximize the catalyst performance [12]. Recently the benefits of introducing mesopores into zeolite crystals by carbon templating have been demonstrated [39–43]. The mesoporous zeolite crystals combine the shape-selectivity, hydrothermal stability and high acidity typical for conventional zeolites with highly efficient transport of reactants and products typical for mesoporous materials. However, in spite of numerous advantages, the carbon templating method has never been implemented industrially, due to several practical challenges including versatility in terms of zeolite structure and compositions, feasibility of tailoring the hierarchical features and ease of being scaled up in a cost-effective way [30].

Here we report the recent progress on synthesis of mesoporous zeolite catalysts modified with nickel nanoparticles using a simple and versatile procedure by *in situ* formation of the carbon template. This novel approach has several advantages in comparison with existing carbon templating methods, where relatively complicated preparative strategies involving multistep impregnation procedures are used. Furthermore, the conventional carbon templating approach often relies on relatively expensive starting materials such as carbon black pearls and tetraethylorthosilicate [14]. In the presented approach a cheap and available silica source – silica gel ( $\text{SiO}_2$ ) is used. Moreover, the carbon template is generated *in situ* by decomposition of methane, which results in the formation of large amounts of coke around the silica supported nickel nanoparticles. The formation of coke over metal nanoparticles is a well-known phenomenon for a range of catalytic reactions that is frequently investigated [44]. In the presented method, the formation of coke is used to serve as carbon template during the subsequent zeolite synthesis. This approach is based on the assumption that the encapsulated carbon is removed by combustion after the zeolite crystallization, thereby creating additional porosity in the zeolite crystals. In Fig. 1 a schematic overview of the presented synthesis approach is given.

By subjecting the metal nanoparticles to a varied amount of methane, the ratio of coke to silica can be tuned. In principal, this may be used to control the porosity in the mesoporous zeolites in a very simple manner. Furthermore, this synthesis method allows adjusting the acidity of the zeolites, i.e. the Si/Al ratio independently of the mesoporosity. Finally, an important advantage of this approach is the relatively versatile synthesis method that in principle allows any desired zeolite with incorporated metal nanoparticles to be prepared in mesoporous form.

In order to compare the conventional and hierarchical zeolite catalysts the cracking and isomerization of the *n*-octane is chosen as a test reaction.

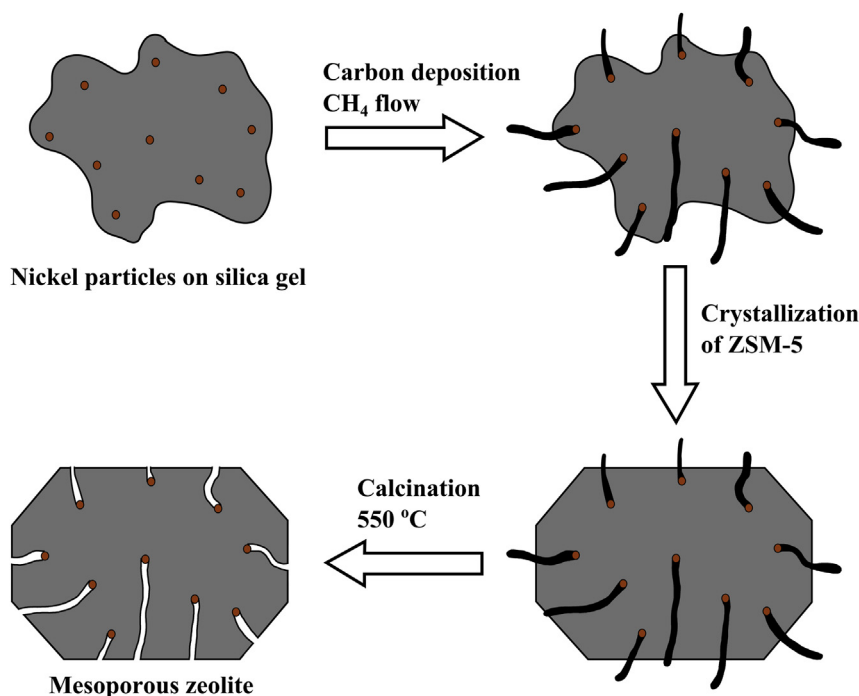
## 2. Experimental

### 2.1. X-ray powder diffraction

X-ray powder diffraction patterns were recorded in transmission mode using Cu-K $\alpha$  radiation from a focussing quartz monochromator and a Huber G760 Guinier camera in the  $2\theta$  interval 5–80°.

### 2.2. Nitrogen physisorption

Nitrogen adsorption and desorption measurements were performed at liquid nitrogen temperature on a Micromeritics ASAP 2020. The samples were outgassed in vacuum at 200 °C during 18 h prior to measurement. Total surface area was calculated according to the BET method. Micropore volumes ( $V_{\text{micro}}$ ) were determined using *t*-plot method. The total sorbed volume ( $V_{\text{total}}$ ), including adsorption in the micropores and mesopores and on the external surface, were calculated from the amount of nitrogen adsorbed at relative pressure  $p/p_0 = 0.99$ , before the onset of interparticle



**Fig. 1.** Overview of the synthesis process: by passing methane over nickel nanoparticles (orange), supported on silica (grey), a carbon template is generated *in situ* as the methane decomposes to coke (black). The obtained carbon-silica composite is then transformed into zeolite during crystallization, incorporating the nickel nanoparticles and carbon. Combustion of the carbon template results in a mesoporous zeolite containing nickel nanoparticles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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