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Article

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Stabilization of Metal Nanoparticle Catalysts via Encapsulation in Mesoporous Zeolites by Steam- Assisted Recrystallization

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Keywords: encapsulated nanoparticles, mesoporous zeolites, methanation, hydrogenation, steam-
assisted recrystallization.

Abstract: Zeolite encapsulated metal nanoparticle catalysts hold great promise for several green
and sustainable processes, ranging from environmental remediation to renewable energy and
biomass conversion. In particular, the microporous zeolite framework keeps the nanoparticles in a
firm grip that can control selectivity and prevent sintering at high temperatures. While progress in
the synthesis of mesoporous zeolites continues, the encapsulation of metal nanoparticles remains
a challenge that often requires complex procedures and expensive additives. Here, we report a
general method to encapsulate both base and noble metal nanoparticles inside the internal voids of
a compartmentalized mesoporous zeolite prepared by carbon templating and steam-assisted

recrystallization. This results in a remarkable shell-like morphology that facilitates the formation of small metal nanoparticles upon simple impregnation and reduction. When the materials are applied in catalysis, we for instance demonstrate that zeolite encapsulated Ni nanoparticles are highly active, selective and stable catalysts for CO₂ methanation (49% conversion with 93% selectivity at 450°C). A reaction where catalysts often suffer from sintering due to the high reaction temperatures. While the introduction of Ni nanoparticles prior to the steam-assisted recrystallization results in the formation of inactive nickel phyllosilicates, noble metals such as Pt do not suffer from this limitation. Therefore, we also demonstrate the synthesis of an active catalyst prepared by the formation of Pt nanoparticles prior to the shell synthesis. We tested the zeolite encapsulated Pt nanoparticles for hydrogenation of linear and cyclic alkenes with increased chain length. The catalysts are active for hydrogenation of oct-1-ene (66% conversion) and cyclooctene (79% conversion) but inactive for the large cyclododecane (<1% conversion), which show that this type of catalyst is highly selective in size selective catalysis. All catalysts are characterized by XRD, TEM, XPS and N₂ physisorption.

1. Introduction

Zeolites have many remarkable properties and find extensive use in heterogeneous catalysis.^{1,2} They are well-known for their Lewis and Brønsted acidity^{3,4} as well as their ability to encapsulate cations, complexes and metals in their crystalline microporous framework⁵⁻⁷. In the particular case of metal nanoparticles, there may be several reasons to encapsulate them inside zeolites. For instance, the zeolite framework may control the nanoparticle size, which results in a high metal dispersion. The zeolite framework may also protect the nanoparticles against sintering caused by particle migration and coalescence⁸⁻¹⁰ or impose a strict size and shape selectivity by excluding

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3 molecules (reactants, intermediates or products) that are too large to diffuse in and out of the
4 zeolite.^{5,11–14} Furthermore, zeolite encapsulated metal nanoparticles may benefit from the unique
5 metal-support interface that is in close proximity to the active sites of the zeolite framework.¹⁵
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10 Although many of the properties of zeolites relates to their microporous framework, the
11 micropores may also cause limitations when it comes to large or bulky substrates. If the substrates
12 and products are about the same size as the micropores, they will constantly be in contact with the
13 pore wall, which will slow down the diffusion. For this reason, the rate of diffusion within a zeolite
14 can be orders of magnitude lower than both molecular and Knudsen diffusion.¹⁶ It is important to
15 underline that the problem of diffusion is the same whether the reaction occurs on an acidic or
16 metal active site inside the zeolite catalyst.
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20 In general, there are two approaches to overcome diffusion limitations. The first approach is to
21 increase the effective diffusivity by increasing the pore size of the zeolite. Over the last 20 years,
22 much effort has therefore been devoted to the synthesis of large- and extra-large pore zeolites.¹⁷
23 The second approach is to decrease the mean diffusion path length, either by decreasing the size
24 of the zeolite crystals¹⁸ or by introducing an additional system of mesopores.^{19–22} The method to
25 synthesize mesoporous zeolites typically includes dealumination,^{23,24} desilication^{21,25–27} or
26 templating using either hard^{28–32} or soft templates.^{33–36}
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30 Despite great technological, environmental and economic interest, general methods for the
31 encapsulation of metal nanoparticles in zeolites are still not well established. In general, the poor
32 diffusion of solvated metal precursors in small- and medium-pore zeolites (8- and 10-membered
33 rings, respectively) preclude post-synthetic encapsulation by simple methods such as
34 impregnation and ion exchange,^{5,37} whereas the incorporation of metal nanoparticles during
35 crystallization often rely on expensive additives or complicated reaction procedures.^{10,38–40}
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Encapsulation of metal nanoparticles *in situ* in microporous zeolites have been accomplished by several research groups which provide the size selectivity from the zeolite network^{37–40}. The encapsulation of metal nanoparticle in mesoporous zeolite catalysts is an area of much ongoing research.^{13,41–45} For instance, Laprune *et al.*⁴² recently encapsulated nickel phyllosilicates in multi-hollow silicalite-1 crystals. The encapsulated nickel phyllosilicates were then reduced to Ni nanoparticles and tested for methane steam reforming at 700 °C. Although the encapsulated Ni nanoparticles showed a high stability against sintering, the researchers also concluded that the catalytic activity of the encapsulated Ni nanoparticles suffered from poisoning by amorphous silica species remaining from the synthesis. Additionally, Li *et al.*⁴⁶ developed a way to encapsulated Pt in a macroporous nanoreactor with a microporous yolk-shell by first impregnating a conventional silicalite-1 zeolite which then could undergo recrystallization to provide the encapsulated Pt in the macroporous interior of the zeolite providing sinter-stable nanoparticles. Generally, supporting metals in open mesopores enhance diffusion of molecules compared to conventional zeolites, however, it results in a lower size/shape selectivity for the reaction when compared to microporous zeolites⁴⁷. Due to the size of the channels, introduction of the solvated metal precursors in mesopores by simple impregnation is easier compared to medium and small pore zeolites. Gu *et al.*⁴⁸ exploited the mesopores in a ZSM-5 zeolite to encapsulate Pt nanoparticles and then convert it into a microporous zeolite to provide size selective catalysis.

In our work, we present a general method to encapsulate metal nanoparticles inside a highly mesoporous zeolite interior with a microporous zeolite shell providing both size selectivity and sinter-stable metal particles. The mesoporous zeolite was prepared by carbon templating, which

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3 allowed for easy impregnation with metal precursors. Formation of a microporous shell with
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5 preservation of the highly mesoporous interior was accomplished by steam-assisted
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7 recrystallization resulting in the remarkable compartmentalized zeolite. The synthesis allowed
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9 for supporting metal nanoparticles in a highly mesoporous interior while still benefitting from
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11 the micropores in the shell. Compared to conventional zeolite synthesis, steam-assisted
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13 crystallization also provides an attractive method to increase the yield, produce less waste and
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15 avoid phase separation.^{49–51} We demonstrate the successful encapsulation of both base and noble
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17 nanoparticles (Ni and Pt, respectively) and show the effect of supporting the metal both before
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19 and after the steam-assisted recrystallization. We tested the Ni containing zeolites in CO₂
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21 methanation, which is a promising power-to-gas technology, but suffers from sintering of metal
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23 particles at the high operating temperatures¹⁵. Here, we showed that encapsulation in the zeolite
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25 with the shell result in the most active with sinter-stable Ni particles.
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31 The shell encapsulated Pt nanoparticles were tested for the size-selective hydrogenation of
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33 linear and cyclic alkenes and showed that the catalyst is highly selective in size selective
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35 catalysis. Figure 1 shows a schematic outline of the method.
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Figure 1. Schematic outline of a general method to encapsulate metal nanoparticles in zeolites.

2. Experimental section

Synthesis of mesoporous ZSM-5 and silicalite-1 (S-1): Following the procedure by Jacobsen *et al.*,²⁹ a pre-dried carbon template (Carbon Black Pearls, BP2000, 2 g) was impregnated with an aqueous solution of tetrapropylammonium hydroxide (TPAOH, 1 M, 7.2 ml) in a Teflon beaker. For ZSM-5, NaAlO₂ (0.016 g) was dissolved in the TPAOH solution prior to impregnation. The impregnated carbon template was left to dry at room temperature overnight. The template was then impregnated with TEOS (4.4 mL) and left to dry at room temperature overnight once more. The beaker with the carbon-silica composite materials was then placed inside a Teflon lined stainless steel autoclave filled with 15 ml distilled water for the steam-assisted synthesis. The autoclave was heated to 180 °C and kept for 72 h. After cooling to room temperature, the solid material was collected by filtration and washed with water until neutral pH. The samples were dried at 80 °C

for 12 h and finally calcined at 550 °C for 20 h to obtain a fine white solid product (meso-S1 or meso-ZSM-5).

Steam-assisted recrystallization (synthesis of recryst-ZSM-5 and recryst-S1): meso-ZSM-5 or meso-S1 (0.5 g) was ground in a mortar, impregnated with varying amounts of TPAOH and dried at room temperature overnight. The dry zeolites were then impregnated with varying amount of TEOS and dried at room temperature overnight once more. The exact amounts and ratio of zeolite to TPAOH and TEOS are listed in Table 1. The dried zeolites were then placed in a Teflon beaker inside a Teflon lined stainless steel autoclave containing 15 ml of water for the steam-assisted recrystallization. The autoclave was heated at 180 °C for 72 h. The product was collected by filtration, washed with water until neutral pH, dried at 80 °C for 12 h and finally calcined at 550 °C for 20 h to obtain a fine white product.

Encapsulation of metals (approach I): As-synthesized meso-S1 or meso-ZSM-5 were dried in a vacuum oven at 60 °C overnight and then impregnated to incipient wetness with an aqueous solution of either $\text{Ni}(\text{NO}_3)_2$ (for a 5 wt% Ni zeolite) or H_2PtCl_6 solution (for a 1 wt% Pt zeolite). The impregnated samples were then dried at 80 °C for 12 h. The nickel-containing meso-ZSM-5 was calcined at 550 °C for 2 h to obtain $\text{NiO}_x/\text{meso-ZSM-5}$, while the platinum-containing meso-S1 was first calcined at 350 °C for 2 h with a 0.5 °C/min ramp in a muffle oven to achieve $\text{PtO}_x/\text{meso-S1}$. The metal oxide-containing sample was then subjected to steam-assisted recrystallization to grow a shell around the $\text{NiO}_x/\text{meso-ZSM-5}$ or $\text{PtO}_x/\text{meso-S1}$. The shell was grown according to the procedure described above using 0.5 g zeolite, 1.8 mL TPAOH and 1.1 mL TEOS. The calcination was limited to 4 h calcination at 550 °C. The calcined Ni-containing zeolite was reduced under 10% H_2 in N_2 at 750 °C for 2 h with a 5 °C /min ramp to obtain

Ni@recryst-ZSM-5(I). The calcined Pt zeolite was reduced under hydrogen at 600 °C for 3 h with a 5 °C /min ramp to obtain Pt@recryst-S1(I). For encapsulation of Ni and Pt in meso-ZSM-5 and meso-S1, respectively, the Ni was reduced under 10% H₂ in N₂ at 500 °C for 2 h with 5 °C /min ramp after impregnation and drying at 80 °C to obtain Ni/meso-ZSM-5 while Pt was reduced under hydrogen at 600 °C for 3 h with 5 °C /min ramp after calcination at 350 °C to obtain Pt/meso-S1.

Encapsulation of metals (approach II): The recryst-S1 and recryst-ZSM-5 zeolite were impregnated with H₂PtCl₆ and Ni(NO₃)₂ solution, respectively, to incipient wetness after drying in a vacuum oven at 60 °C overnight. Afterward the samples were dried at 80 °C for 12 h. The Ni sample was reduced under 10% H₂ in N₂ at 500 °C for 2 h with a 5 °C /min ramp to obtain Ni@recryst-ZSM-5(II). The platinum-containing zeolite was first calcined at 350 °C for 2 h with a 0.5 °C/min ramp in a muffle oven (PtO_x@recryst-S1(II)) and then reduced under hydrogen at 600 °C for 3 h with 5 °C /min ramp to obtain Pt@recryst-S1(II).

Results and discussion

Figure 2, Table 1, and Figure S1-S5 compiles the results from N₂ physisorption and X-ray powder diffractions (XRPD) analysis of all the prepared support materials. In particular, the table shows the effect on the surface area and porosity by changing the ratio of TPAOH and TEOS during the steam-assisted recrystallization of the carbon templated mesoporous zeolites. In general, the addition of TEOS slightly decreased the total pore volume, while the surface area and micropore volume remained in the same range under all conditions. A significant increase in surface area and

micropore volume was observed by the addition of large amounts of both TPAOH and TEOS in Entry 5.

Table 1. Outline of the prepared zeolites, the synthesis conditions and the results from N₂ physisorption analysis.

#	Sample	TPAOH ^a	TEOS ^b	Surface area ^c (m ² /g)	Pore volume ^d (cm ³ /g)	Micropore volume ^e (cm ³ /g)
1	meso-S1	-	-	453	0.35	0.14
2	recryst-S1(1:0)	1	-	449	0.32	0.13
3	recryst-S1 (1:1)	1	1	422	0.30	0.13
4	recryst-S1 (2:0)	2	-	451	0.33	0.12
5	recryst-S1 (2:2)	2	2	530	0.30	0.16
6	meso-ZSM-5	-	-	432	0.30	0.13
7	recryst-ZSM-5	1	1	440	0.31	0.09

[a] 1=3.6 mL and 2=7.2 mL 1 M TPAOH to 1 g of meso-S1/meso-ZSM-5 [b] 1= 2.3 mL and 2=4.6 mL TEOS to 1 g of meso-S1/meso-ZSM-5 [c] calculated by the BET method [d] calculated at relative pressure p/p₀=0.95 [e] calculated by the *t*-plot method.

More detailed information about the morphology of the recrystallized zeolites is evident from the physisorption isotherms and the pore size distributions shown for meso-S1, recryst-S1(1:0) and recryst-S1(1:1) in Figure 2A and Figure S2, respectively.

Figure 2. A) N₂ physisorption isotherms of meso-S1 (black), recryst-S1(1:0) (red) and recryst-S1(1:1) (blue) and B) hysteresis scan of recryst-S1(1:1)

As expected, the physisorption isotherms of all zeolites in Figure 2A show significant adsorption of N₂ at low relative pressures ($p/p^\circ < 0.01$) which is typical for microporous zeolites. Furthermore, all three isotherms show a significant hysteresis loop at higher relative pressures. For meso-S1 (black), the hysteresis loop closes at around $p/p^\circ = 0.85$, which indicates the presence of large and open mesopores^{52,53}. According to the IUPAC classification⁵⁴, the physisorption isotherm of meso-S1 is a type IV with an H1 hysteresis loop. Figure S2 shows the corresponding pore size distribution as calculated by BJH analysis of the desorption branch and shows that the carbon templating result in a broad distribution of mesopores around between 10-34 nm in diameter. This result is in good agreement with previous reports^{29,55}. In contrast, the hysteresis loops of recryst-S1(1:0) and recryst-S1(1:1) (red and blue, respectively) modified by steam-assisted recrystallization are almost parallel until the forced closure point at around $p/p^\circ = 0.45$. According to the IUPAC classification, these data correspond to type IV isotherms with type H2a hysteresis loops. This behavior indicates that the recrystallized zeolites have an inkbottle type porosity with a constricted system of internal voids and mesopores that are only accessible via the inherent

zeolite micropores.^{53,56} It is important to mention that the peaks around 3.8 nm in the pore size distribution are not related to actual mesopores, but simply caused by cavitation and the so-called tensile strength effect at the forced closure point.^{57,58} As expected, the same peaks are not evident from the corresponding pore size distribution as calculated from the adsorption branch (data not shown). While the change from type H1 to type H2a hysteresis loops indicate the successful synthesis of a microporous zeolite shell, the physisorption analysis also reveals that both TPAOH and TEOS are required to transform all open mesopores into fully enclosed compartments. While recryst-S1(1:0) has a total pore volume of 0.32 g/cm³ and BJH analysis indicates some remaining open porosity in the mesoporous range, recryst-S1(1:1) has a total pore volume of 0.30 g/cm³ and a relatively flat desorption branch until the forced closure point at $p/p^{\circ}=0.45$. Figure 2B shows the isotherms from a hysteresis scanning experiment performed on recryst-S1(1:1) to investigate the desorption branches at different partial pressures and degrees of filling in more detail. As expected, the flat shape of the desorption scans confirm that all the mesopores empty via cavitation controlled evaporation rather than pore blocking.^{52,59,60}

Figure S1 shows the XRPD analysis of meso-S1, recryst-S1(1:0) and recryst-S1(1:1), respectively. The diffraction patterns of all other zeolite materials are shown in Figure S3. In general, the diffraction patterns show no significant differences between the parent and modified zeolites. This confirms that both carbon templating and steam-assisted recrystallization result in zeolites with the expected MFI structure and good crystallinity.⁶¹ Furthermore, the diffraction patterns show no significant differences between the recrystallized samples prepared with different ratios of zeolite, TPAOH and TEOS, which is in good agreement with the results from N₂ physisorption analysis reported in Table 1.

Figure 3 shows an SEM and TEM image of meso-S1 and recryst-S1(1:1), respectively. The SEM images show that the crystal size of both samples is around 1-2 μm , which confirms that the added TEOS crystallizes on the surface of the carbon templated zeolites rather than in new separate crystals. We therefore speculate that the carbon templated zeolite may function as effective seed crystals in this step. Furthermore, the SEM images show a significant difference in the surface features of the two samples. While the surface of meso-S1 appears fluffy, which is typical for mesoporous zeolites and in good agreement with previous reports,^{13,19,62,63} the surface of recryst-S1(1:1) appears more smooth with well-defined terraces. The same features are also evident from the TEM images, which also reveal more insight into the nature of the enclosed mesopores. While Figure 3C clearly shows the open porosity of the carbon-templated zeolite, Figure 3D exhibits how the steam-assisted crystallization has restructured the surface of the zeolite and transformed the open porosity into a large number of small and separate compartments. The thickness of the zeolite shell is typically in the range of 10-30 nm.

Figure 3. SEM and TEM images of meso-S1 (A+C) and recryst-S1(1:1) (B+D)

Based on our previous experience with encapsulated metal nanoparticles, we speculated if the steam-assisted recrystallization could offer a general method to encapsulate both base and noble metal nanoparticles in mesoporous zeolites. We therefore prepared a number of Ni and Pt catalysts by simple impregnation of the metal precursors on the mesoporous zeolites both before and after the steam-assisted recrystallization.

Figure 4 shows the TEM images of the Ni catalysts together with their corresponding particle size histogram fitted with a log-normal distribution. For comparison, Ni/meso-ZSM-5 was prepared by impregnation of carbon-templated meso-ZSM-5, Ni@recryst-ZSM-5(I) was prepared by impregnation of carbon-templated meso-ZSM-5 followed by steam-assisted recrystallization and Ni@recryst-ZSM-5(II) was prepared by steam-assisted recrystallization of meso-ZSM-5 followed by impregnation. The nickel-containing catalysts were reduced under the as-mentioned conditions (please see experimental section).

The first TEM image in Figure 4 shows that a number of large Ni nanoparticles (up to 46 nm) were present on the external surface of Ni/meso-ZSM-5, which resulted in a relatively broad particle size distribution. In contrast, less Ni nanoparticles were present on the external surface area of Ni@recryst-ZSM-5(I) and Ni@recryst-ZSM-5(II), which resulted in smaller nanoparticles and more narrow size distributions. Furthermore, the TEM images also show that the enclosed porosity appeared to encapsulate a significant number of the Ni nanoparticles within the zeolite shell. The XRPD patterns of the three Ni catalysts are shown in Figure S6 in the supporting information. Besides the characteristic diffraction pattern of ZSM-5, the XRD analysis also reveal some small peaks from Ni(111). Although the signals are too weak to confirm the average particle size by line broadening analysis, the results indicate that the Ni nanoparticles decrease in the order of Ni/meso-ZSM-5>Ni@recryst-ZSM-5(II)>Ni@recryst-ZSM-5(I).

Figure 4. TEM images of A) Ni/meso-ZSM-5, B) Ni@recryst-ZSM-5(I) and C) Ni@recryst-ZSM-5(II) together with their particle size distributions based on the measurement of >100 nanoparticles.

In order to compare the catalytic activity, we tested the Ni catalysts for high-temperature CO_2 methanation, which is an important reaction that is well known to suffer from sintering.^{64–66} Figure 5 A, B, and C show the molar fraction of CH_4 , CO and CO_2 as a function of the reaction temperature. A comparison of the product distribution at 450 °C shows that Ni@recryst-ZSM-5(II) results in 49% conversion and 93% selectivity, which is significantly higher than the other catalysts. Considering the similar particle size distributions of Ni@recryst-ZSM-5(II) and Ni@recryst-ZSM-5(I), we speculate that the alkaline and hydrothermal conditions under the steam-assisted recrystallization could result in the formation of nickel phyllosilicates

(see Figure S10). It has previously been shown that these phyllosilicates are difficult to reduce into Ni nanoparticles and may decrease the catalytic activity.^{6,42} Approach II (post-impregnation) does not suffer from the formation of these inactive species and is therefore the most effective method to encapsulate base metals such as Ni nanoparticles.

Figure 5. Product distribution as a function of the temperature for A) Ni/meso-ZSM-5, B) Ni@recryst-ZSM-5(I) and C) Ni@recryst-ZSM-5(II) together with a summary of the catalytic activity at 450 °C.

Figure 6 shows the catalytic activity of Ni/meso-ZSM-5 compared to Ni@recryst-ZSM-5(II) over 50 h at 450 °C. The results clearly show that Ni@recryst-ZSM-5(II) not only results in higher conversion and selectivity, but also in higher stability over time.

Figure 6. Catalytic stability for A) Ni/meso-ZSM-5 and B) Ni@recryst-ZSM-5(II) over 50 h at 450 °C.

Figure S12 shows the results from the TEM analysis of the spent catalysts after 50 h at 450 °C. The TEM image of Ni/meso-ZSM-5 shows the formation of large Ni nanoparticles on the surface of the catalysts, which indicates that severe sintering may explain the poor stability. In contrast, the TEM image of Ni@recryst-ZSM-5 shows that the zeolite-encapsulated nanoparticles appear to remain within the confined space of the small zeolite compartments. This indicates that the zeolite shell effectively prevents nanoparticle migration and coalescence on the surface of the catalyst, which results in a higher metal dispersion, a higher catalytic activity and higher thermal stability.

In order to investigate if noble metal nanoparticles could be encapsulated by impregnation of the carbon-templated zeolite prior to the steam-assisted recrystallization, we then prepared Pt/meso-S1 and Pt@recryst-S1(I). As expected, the XRPD analysis shows the characteristic diffraction pattern of the MFI zeolite as well as an additional peak from Pt(111) at 39.6° ⁶⁷, see Figure S15. Figure S17 shows the XPS analysis for the Pt 4f orbitals in Pt/meso-S1 and Pt@recryst-S1(I), respectively. The difference in signal intensity indicates that significantly more Pt is present on the surface of Pt/meso-S1 than on the surface of Pt@recryst-S1(I). For comparison, ICP-OES analysis showed that the metal loading of Pt/meso-S1 and Pt@recryst-S1(I) was 0.8% and 0.7%, respectively. Since the change in metal loading can only account for 12.5% of the decrease in signal intensity, we assign the rest of the decrease to a successful encapsulation of the Pt nanoparticles.

Figure 7 shows two representative STEM images of the Pt catalysts (please see Figure S18 and S19 for more images). With the exception of a few larger nanoparticles on the surface of the catalyst, the STEM analysis shows that a large number of small nanoparticles are still present on Pt@recryst-S1(I) after the steam-assisted recrystallization.

Figure 7: STEM images of Pt/meso-S1 (A) and Pt@recryst-S1(I) (B).

In order to investigate the degree of encapsulation and the potential use for selective catalysis, we tested the two Pt catalysts for the shape-selective hydrogenation of linear and cyclic alkenes. The results in Table 2 clearly show that encapsulation of the Pt nanoparticles had a significant effect on the catalytic activity. As expected, the effect is most pronounced for cyclododecene, which is too large to enter the microporous zeolite. These results therefore confirm that the recrystallized zeolite encapsulates a large fraction of the Pt nanoparticles. For the two smaller molecules, 1-octene and cyclooctene, the decreased activity may be explained by a slower diffusion^{5,48}. In order to investigate the effect of the preparation procedure, we also tried to encapsulate the Pt nanoparticle after the steam-assisted recrystallization (Pt@recryst-S1(II)), please see supporting information. This, however, resulted in a significantly lower size selectivity (see Table S2), which indicates an incomplete encapsulation of the Pt nanoparticles (Figure S20). For this reason, it appears that Approach I (pre-impregnation) is the more effective method to encapsulate noble metals such as Pt nanoparticles.

Table 2. Catalytic results from the hydrogenation of alkenes^a

Catalyst	Substrate	Product	Time	Conversion ^b
Pt/meso-S1	oct-1ene	octane	1 h	99%
	cis-cyclooctene	cyclooctane	1 h	99%
	cyclododecene	cyclododecane	24 h	53%
Pt@recryst-S1(I)	oct-1ene	octane	1 h	6%
	oct-1ene	octane	24 h	66%
	cis-cyclooctene	cyclooctane	1 h	8%
	cis-cyclooctene	cyclooctane	24 h	79%
	cyclododecene	cyclododecane	24 h	1%

[a] Reaction conditions: alkene (1 mmol), catalyst (50 mg), decane (internal standard, 0.2 mmol), ethyl acetate (5 mL), 1 bar H₂ room temperature [b] Conversion determined by GC-FID.

Conclusion

A general steam-assisted recrystallization method was developed to encapsulate both base and noble metal nanoparticles inside the internal voids of compartmentalized mesoporous ZSM-5 or silicalite-1. For full coverage of mesoporous zeolite with a microporous layer, both TEOS and TPAOH were required. It was shown that encapsulated Ni nanoparticles, where Ni was introduced after steam-assisted recrystallizations (Approach II), was the most active and stable catalyst for CO₂ methanation with a site time yield of 283 mol CH₄/mol Ni h⁻¹. Whereas, the zeolite encapsulated Ni nanoparticles prepared according to approach I suffer from the possible formation of inactive nickel phyllosilicates. Approach II offers a suitable way to obtain sinter-stable encapsulated base metals which can be used for high temperature reactions.

Furthermore, it was demonstrated that the Pt catalyst prepared by introducing the Pt nanoparticles prior to the steam-assisted recrystallization (approach I), was more size-selective in linear and cyclic alkenes hydrogenation, and prove that the method is highly applicable for obtaining size selective catalysts. Therefore, we conclude that approach I is more effective for encapsulation of noble metals while approach II is more effective for encapsulation of base metals. The general method offers a new way for encapsulation of metals in hierarchical zeolite catalysts.

ASSOCIATED CONTENT

Supporting Information. Experimental characterization conditions, materials used for synthesis, reaction conditions and analysis for hydrogenation of alkenes and methanation, XRPD and N₂ physisorption of samples for shell optimization, XRPD and TEM images of Ni zeolites

before and after stability test, XRPD and STEM images of Pt zeolites, textural properties of Pt@recryst-S1(II), XPS of Pt zeolites, catalytic results of Pt@recryst-S1(II) (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

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Figure 10: For Table of Contents Only

Schematic outline of a general method to encapsulate metal nanoparticles in zeolites.

305x164mm (300 x 300 DPI)

A) N₂ physisorption isotherms of meso-S1 (black), recryst-S1(1:0) (red) and recryst-S1(1:1) (blue) and B) hysteresis scan of recryst-S1(1:1).

SEM and TEM images of meso-S1 (A+C) and recryst-S1(1:1) (B+D).

TEM images of A) Ni/meso-ZSM-5, B) Ni@recryst-ZSM-5(I) and C) Ni@recryst-ZSM-5(II) together with their particle size distributions based on the measurement of >100 nanoparticles.

Product distribution as a function of the temperature for A) Ni/meso-ZSM-5, B) Ni@recryst-ZSM-5(I) and C) Ni@recryst-ZSM-5(II) together with a summary of the catalytic activity at 450 °C.

Catalytic stability for A) Ni/meso-ZSM-5 and B) Ni@recryst-ZSM-5(II) over 50 h at 450 °C.

STEM images of Pt/meso-S1 (A) and Pt@recryst-S1(I) (B).

338x190mm (300 x 300 DPI)