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CoFe₂O₄ Nanocrystals Mediated Crystallization Strategy for Magnetic Functioned ZSM-5 Catalysts

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Abstract: Zeolites have many applications in the petrochemical and fine chemical industry and their functionalization does expand the spectrum of potentials. However, the integration of functional nanocrystals into zeolite frameworks with controlled size, dispersion and crystallization behavior still remains a significant challenge. Here, we report a new synthesis of magnetic functioned ZSM-5 zeolite catalysts *via* a CoFe₂O₄ nanocrystal mediated crystallization strategy. We found that high crystallinity of CoFe₂O₄ nanocrystals results in a well-dispersed encapsulation of them into a single-crystal of ZSM-5 due to non-further-grown nanocrystals during the fast ZSM-5 growth. On the contrary, low crystallinity of CoFe₂O₄ nanocrystals leads to the polycrystalline zeolite growth due to the secondary growth of nanocrystals accompanied by the zeolite crystallization and large lattice mismatch between them. The successful encapsulation of small CoFe₂O₄ nanocrystals (~ 4 nm) into single crystals lies on the pre-attachment of them into solid silica gel. During the growth of ZSM-5

crystals, no secondary growth of nanocrystals happens and its motion is restricted. The encapsulation of magnetic CoFe_2O_4 nanocrystals not only endows magnetic function into zeolites for the first time, but also does not impact catalytic performance of ZSM-5 in acetalization of cyclohexanone with methanol, which is highly promising in catalytic industries.

1. Introduction

The significance of crystallization process for the design and synthesis of functional nanocomposites has driven multilevel research into the controlled crystal nucleation and growth.^[1-4] Among them, the crystallization of one host phase with the coalescence of another guest species (e.g. ion complexes, nanocrystals)^[5, 6] has been recognized as a widespread method to achieve multifunctional materials with tunable structure and properties.^[7-9]

Zeolites, microporous crystalline aluminosilicates, have been widely applied in the fields of adsorption, separation, and catalysis in petrochemical and chemical industry.^[10-18] Aiming to the functionalization of host zeolite matrixes, various guest species are added into the precursor of zeolites, in which the nucleation and growth of zeolite crystals occur together with guest species.^[19-26] Chen and coworkers^[27] have successfully introduced Pd nanoparticles inside mesoporous MFI zeolite nanocrystals thorough a modified Kirkendall growth process. Yu and coworkers^[28] reported the synthesis of silicalite-1 with ultra-small Pd clusters confined in the intersectional channels combining a modified Pd ion and the precursor in a hydrothermal process. However, based on these strategies reported previously, the ion complexes are usually trapped into the channels of zeolite frameworks which might result in a poor mass transfer for the applications involving the bulk reactants. Furthermore, the composition of guest species on the zeolite crystallization behaviours is beyond well understood, resulting in little satisfactory control over the assembly of zeolite building blocks. The main reason may be due to the rigidity of zeolite crystals. During the crystallization of the

zeolites from the traditional homogeneous precursors, guest species cannot be easily involved into a thermodynamically-controlled crystal growth. Adding guest species (e.g. ions or nanocrystals) directly into the homogeneous precursors of zeolites usually leads to large and non-uniform nanocrystals as well as poor dispersion and unsatisfactory functional properties. Therefore, exploring new strategies to control zeolite crystallization and endow it useful functions with the coalescence of adjustable nanocrystal properties is a great challenge to achieve the diversity and complexity of nanocomposites.

Here, we report a magnetic functioned ZSM-5 composite from the mediation of cobalt iron oxide (CoFe_2O_4) nanocrystals over the zeolite crystallization.^[29, 30] A mesoporous silica solid gel was selected as a precursor, which acted as a matrix to confine the magnetic CoFe_2O_4 nanocrystals growth. We found that high relative crystallinity of the nanocrystals could result in a successful encapsulation of them into the single crystals of ZSM-5 and endow the zeolites magnetic function, because no further growth of nanocrystals happens during the fast growth of ZSM-5 single-crystal. On the contrary, the nanocrystals with a low relative crystallinity lead the polycrystalline zeolite growth to form microspheres composed of the assembled ZSM-5 nanorods and well-dispersed CoFe_2O_4 at the voids between the zeolite crystals (**Figure 1**) because the secondary growth of nanocrystals accompanied by the zeolite crystallization and large lattice mismatch between them. The successful encapsulation of the small CoFe_2O_4 nanocrystals (~ 4 nm) into ZSM-5 matrixes lies on the pre-attachment of the high crystalline nanocrystals on the pore surface of solid silica gels. During the growth of ZSM-5, no secondary growth of nanocrystals happens and its motion is restricted. The obtained magnetic single-crystal zeolites encapsulated with CoFe_2O_4 nanocrystals possess high magnetization (4.7 emu/g) with superparamagnetic property, a uniform size (~ 9 μm), and high surface area (330 m^2/g). These magnetic single-crystal ZSM-5 catalysts exhibit an excellent conversion, selectivity in the acetalization of cyclohexanone with methanol. The

encapsulation of magnetic CoFe_2O_4 nanocrystals does not impact the catalytic performance of ZSM-5 zeolites, which is highly promising in the chemical and catalytic industries.

2. Results and Discussion

The SEM image (Figure S1) shows that the commercial mesoporous silica solid gels as a precursor have a polyhedral morphology with a uniform size of $\sim 45\ \mu\text{m}$. Through an impregnation strategy, CoFe_2O_4 nanocrystals can be incorporated into the mesopores of the solid silica gels (Figure S2). The obtained $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ composites after being calcined at $600\ ^\circ\text{C}$ are used to prepare the precursors for the growth of zeolite ZSM-5 crystals. After a hydrothermal treatment at the temperature of $180\ ^\circ\text{C}$, the $\text{CoFe}_2\text{O}_4@\text{ZSM-5}$ hybrids are obtained (denoted as $\text{CoFe}_2\text{O}_4@\text{ZSM-5-600}$). The XRD pattern (Figure S3a) of $\text{CoFe}_2\text{O}_4@\text{ZSM-5-600}$ shows typical diffraction peaks, which can be well indexed to zeolite MFI structure, indicating that ZSM-5 phase with a high crystallinity is formed. The SEM image (**Figure 2a**) of the sample $\text{CoFe}_2\text{O}_4@\text{ZSM-5-600}$ demonstrates the coffin-shaped and twin crystal morphology which is commonly formed for zeolites with MFI structure. The particle (inset of Figure 2a) exhibits clear edges, indicating the single crystal structure of ZSM-5. The TEM image (Figure 2d) clearly shows that numerous tiny nanocrystals are well dispersed in the matrix of zeolite crystals. The size distribution curve of CoFe_2O_4 nanocrystals (Figure 2g) displays a mean diameter centred at $\sim 4\ \text{nm}$. The corresponding selected-area electron diffraction (SAED, Figure 2d inset) pattern exhibits a clear single-crystal diffraction characteristic of zeolite ZSM-5 together with polycrystalline diffraction ring of CoFe_2O_4 nanocrystals. Due to the small lattice space of CoFe_2O_4 nanocrystals, its diffraction rings mainly appear at the outer position which is attributed to the lattice plane (511) with a d -spacing of $\sim 0.16\ \text{nm}$. Furthermore, the HRTEM image (Figure S4) also confirms that the tiny CoFe_2O_4 nanocrystals are encapsulated within the zeolite matrix. These results indicate that the involvement of CoFe_2O_4 nanocrystals does not disturb the crystallinity of the host ZSM-5

single crystals. Nitrogen isotherms of the $\text{CoFe}_2\text{O}_4@\text{ZSM-5-600}$ hybrids (Figure S5a) show a sharp uptake at a low relative pressure (P/P_0), indicating the characteristic micropores. At a higher relative pressure, the nearly H2-type hysteresis loop is observed which is ascribed to the intercrystalline mesoporosity stemmed from the introduction of nanocrystals.^[22] The corresponded BET surface areas and pore volumes for the samples are calculated to be 330 m^2/g and 0.20 cm^3/g , respectively.

The $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ composites after being calcined at 400 and 200 °C are also used to prepare the precursors for the growth of zeolite ZSM-5 crystals (donated as $\text{CoFe}_2\text{O}_4@\text{ZSM-5-400}$, $\text{CoFe}_2\text{O}_4@\text{ZSM-5-200}$, respectively) under the same condition with the samples at 600 °C. XRD patterns (Figure S3b and c) show that the samples also possess a high crystallinity of ZSM-5 phase. SEM images of the sample $\text{CoFe}_2\text{O}_4@\text{ZSM-5-400}$ (Figure 2b) and $\text{CoFe}_2\text{O}_4@\text{ZSM-5-200}$ (Figure 2c) show a spherical morphology with a relatively uniform size of $\sim 9 \mu\text{m}$ in diameter. Moreover, the SEM images of the cracked microspheres (the inset in Figure 2b and 2c) reveal that the microsphere is composed of numerous assembled nanorods. TEM images of the $\text{CoFe}_2\text{O}_4@\text{ZSM-5-400}$ (Figure 2e) and $\text{CoFe}_2\text{O}_4@\text{ZSM-5-200}$ (Figure 2f) show that the ZSM-5 nanorods pack together and many nanocrystals are dispersed on these nanorods. The size distribution curve of the CoFe_2O_4 nanocrystals displays a mean diameter centred at ~ 8 and ~ 12 nm for $\text{CoFe}_2\text{O}_4@\text{ZSM-5-400}$ (Figure 2h) and $\text{CoFe}_2\text{O}_4@\text{ZSM-5-200}$ (Figure 2i), respectively. The nanocrystals size change is related to the starting particle crystallinity. The HRTEM images (inset of Figure 2e and 2f) of the cracked microspheres show that lattice fringes of CoFe_2O_4 nanocrystals and ZSM-5 lattice. These results clearly suggest that the CoFe_2O_4 nanocrystals are dispersed in the voids among the ZSM-5 nanorods. These results significantly indicate that the structure of the hybrid $\text{CoFe}_2\text{O}_4@\text{ZSM-5}$ is strongly related to the size of guest nanocrystals which stem from the different calcination for the crystallization of CoFe_2O_4 . The BET surface areas for the samples $\text{CoFe}_2\text{O}_4@\text{ZSM-5-400}$ and $\text{CoFe}_2\text{O}_4@\text{ZSM-5-200}$ are calculated to be 367 and 379,

and the pore volumes are 0.22 and 0.23 cm³/g, respectively (Figure S5b and 5c). The surface area and pore volume of them are a little higher than that of sample CoFe₂O₄@ZSM-5-600. It indicates that the single-crystal ZSM-5 is denser than the polycrystalline microspheres with both microporosity and moderate mesoporosity ascribed to the agglomeration of nanorods.

The composition of precursors for zeolites is important for the crystallization of ZSM-5. The CoFe₂O₄ nanocrystals can be successfully incorporated into the mesopores of the solid silica gel (Figure S6 and S7). The nanocrystals size distribution varies from 12.5 to 4.2 nm as the calcination temperature increased (Figure S6c, S6f and S6i) due to the incomplete decomposition of metal nitrate precursor and restricted solid diffusion in the disordered mesopores of silica gel.^[31] The XRD pattern of the sample (Figure 3B) calcined at 600 °C exhibits well-resolved diffraction peaks indexed to CoFe₂O₄ phase (JCPDS no. 22-1086), indicating a high crystallinity. The relative crystallinity of the CoFe₂O₄ nanocrystals can be decreased to 78 % and 39 % by reducing the calcination temperature from 400 to 200 °C, respectively (Figure 3A), suggesting the mixed metal oxides are existed. The X-ray photoelectron spectroscopy (XPS) spectra of CoFe₂O₄@SiO₂ calcined at 600 °C (Figure S8a and S8b) show typical peaks for Fe2p_{3/2} (724.0 eV), Fe2p_{1/2} (710.0 eV), Co2p_{3/2} (793.8 eV) and Co2p_{1/2} (779 eV) with satellite peaks for the CoFe₂O₄ materials.^[32, 33] As comparable, for the samples after the hydrothermal treatment, the characteristic peaks for Fe³⁺ and Co²⁺ from CoFe₂O₄ materials (Figure S8c and S8d) suggest that no valence change of metal species for CoFe₂O₄ nanocrystals with high crystallinity. For the samples of CoFe₂O₄@SiO₂ calcined at 400 and 200 °C, XPS spectra indicate that the iron and cobalt species from mixed oxide. H₂-temperature-programmed-reduction (TPR) profile (Figure 3C) of the CoFe₂O₄@SiO₂ composites sample calcined at 200, 400, 600 °C all show the characteristic peaks for the reduction of CoO to metallic cobalt (340 ~ 363 °C), Fe₂O₃ to Fe₃O₄ (430 ~ 460 °C) and Fe₃O₄ to FeO and metallic Fe (above 600 °C).^[32, 34] It should be noted that the peaks at the low temperature centred at 180 and 230 °C are ascribed to the reduction of Fe³⁺ and Co²⁺

respectively.^[34] For the sample calcined at 600 °C, the peaks are shifted to higher temperature compared with those of samples calcined at 200 and 400 °C, suggesting that the metal oxides become difficult to be reduced, which is due to the increased crystallinity of nanocrystals and interaction between metal oxides and silica.^[35] In the growth process of ZSM-5 crystals, the metal ions or amorphous metal oxides are not stable and may act as the resource for the secondary growth of CoFe₂O₄ nanocrystals, which is competitive with the crystallization of ZSM-5 crystals. To qualitatively verify this process, chemical hardness of metal ions (Fe³⁺ and Co²⁺), amorphous metal oxide (Fe₂O₃, CoO and SiO₂) and crystalline CoFe₂O₄ nanocrystals were calculated based on Density Functional Theory (DFT) (Table S1).^[36] The crystalline CoFe₂O₄ nanocrystals with the lowest chemical hardness are stable in an alkaline solution. On the other hand, the metal ions and amorphous metal oxides with a higher chemical hardness are not stable^[37] and may further react to form crystalline CoFe₂O₄ nanocrystals in an alkaline condition, which may impact the crystallization behaviour of ZSM-5.

Based on the above observations, we propose a CoFe₂O₄ nanocrystal mediated crystallization strategy for ZSM-5 zeolite composites. In our work, CoFe₂O₄ nanocrystals with different crystallinity that are pre-attached in the mesopores of the silica solid gel precursors lead to the different crystallization behaviours of the zeolites during the hydrothermal process. Generally, conventional coffin-shaped ZSM-5 crystals (Figure S9) are formed if the same silica gel without the CoFe₂O₄ nanocrystals is used. When the guest CoFe₂O₄ nanocrystals are incorporated into the silica gels, the metal ions or the amorphous metal oxides which exist around the CoFe₂O₄ nanocrystals with a lower relative crystallinity provide extra active sites for further CoFe₂O₄ nanocrystals growth via Ostwald rippling process in the alkaline condition. This process makes the pre-attached CoFe₂O₄ nanocrystals further grow during the crystallization process of zeolites. While the crystallization of two phases happens simultaneously, the lattice match between the interfaces normally determine

the size and position of incorporated guest nanocrystals.^[38] The lattice mismatch between the two majority lattice planes of ZSM-5 (plane 101 with *d*-spacing of 1.1 nm) and CoFe₂O₄ (plane 311 with *d*-spacing of 0.25 nm) is up to 77 % (Table S2). Such large lattice mismatch can result in either host polycrystalline or anisotropic structures with segregation of the host and guest species.^[39, 40] In our case, the further-grown CoFe₂O₄ nanocrystals cannot be encapsulated in the ZSM-5 single crystals, resulting in the phase separation from the crystallization of ZSM-5.^[41] Conversely, the CoFe₂O₄ nanocrystals with high crystallinity are so stable and inert that no addition active sites for further growth. Therefore, during the hydrothermal process, only the crystallization of ZSM-5 happens and the lattice mismatch between two phases is not the dominated factor. Due to the initial attachment of small nanocrystals (~ 4 nm) on the pore surface of the solid silica gels and interaction between them, the dynamics of the nanocrystal motion is restricted.^[1, 5] Meanwhile, solid silica gel for heterogeneous precursors and high hydrothermal temperature (180 °C) for zeolite growth are the critical conditions for allowing kinetic-controlled aggregation of zeolite nucleus and fast ZSM-5 crystal growth.^[12, 42] Fast ZSM-5 frameworks growth is prior to the motion of pre-attached and non-further-grown small CoFe₂O₄ nanocrystals. As a result, ZSM-5 growth is inclined to kinetically circumvent small CoFe₂O₄ nanocrystals with decreased internal strain^[43] rather than excluding them from the ZSM-5 single-crystal frameworks. The rigid and inert CoFe₂O₄ nanocrystals are supposed to be involved into the fast crystallization process of ZSM-5 and no phase separation happens. In such systems, the structural differences may be accommodated even though a distinct mismatch between the lattice planes of the two phases is existed.^[44] Consequently, the small CoFe₂O₄ nanocrystals can be encapsulated into the zeolite single crystals. In sum, through controlling the relative crystallinity of pre-attached guest nanocrystals in the mesoporous solid silica gels, the ZSM-5 crystallization behaviours can be tuned from the polycrystalline to single crystalline with desired function.

The saturation magnetization values at room temperature for the samples CoFe₂O₄@ZSM-5-600, CoFe₂O₄@ZSM-5-400, CoFe₂O₄@ZSM-5-200 are measured to be 4.7, 1.2 and 0.6 emu/g, respectively (Figure 4A and S10). During the hydrothermal treatment, the metal ions/amorphous metal oxide further grow into crystalline metal oxide. However, their crystallinity of nanocrystals is still lower than that of CoFe₂O₄@ZSM-5-600, leading to the decreased magnetization values.^[45, 46] The hysteresis loops recorded at 5 K (Figure 4B) shows that the coercivity of the samples CoFe₂O₄@ZSM-5-600, CoFe₂O₄@ZSM-5-400, CoFe₂O₄@ZSM-5-200 is 12232, 2516, 1305 Oe and the remanence is 5.2, 1.06, 0.56 emu/g, respectively. These values are increased with the enforcement of crystallinity. The zero field cooling (ZFC) curve (Figure 4C) for the sample CoFe₂O₄@ZSM-5-600 composites shows a main plateau around 285 K, suggesting that the blocking temperature is in the room temperature range. It should be noticed that a peak at 10.5 K is observed, indicating that some magnetic ordering transition happens.^[47] The ordering transition temperature (T_O) is also related to the particle size of the CoFe₂O₄ nanocrystals by an equation (1):

$$T_O = KV/25k_B \quad (1)$$

where k_B is the Boltzmann constant (1.38×10^{-16} erg K⁻¹), K is the anisotropy constant (1.2×10^6 erg cm⁻³) and V is volume of the particle.^[48] The diameter of the CoFe₂O₄ particles is calculated to be ~ 4 nm, which is close to the data from the TEM images. As a comparison, there is no peak in ZFC curve (Figure 4D) of pure CoFe₂O₄ materials (Figures S11 and S12). It is well known that CoFe₂O₄ materials are widely used in magnetic fluids, magnetic resonance imaging (MRI) contrast, *etc.* due to its intrinsic coercivity other than the superparamagnetic property.^[49-55] Here, for the first time, a crystalline framework zeolite ZSM-5 is used to encapsulate the magnetic CoFe₂O₄ nanocrystals with defined size and shape, achieving the superparamagnetic property.

The excellent magnetic properties of the CoFe₂O₄@ZSM-5 composites make them excellent candidates for various applications such as adsorption and catalysis due to its easy

manipulation. The key feature is whether the encapsulation of magnetic CoFe_2O_4 nanocrystals could impact the catalytic performance. Here, we apply the acetalization of cyclohexanone with methanol (**Figure 5A**) to validate the catalytic performance of the composite $\text{CoFe}_2\text{O}_4@\text{ZSM-5-600}$. The acetalization reaction between ketone and alcohol is an important organic synthetic route which has been widely employed in industrial process for the production of drug intermediate and target fine chemicals.^[56] The magnetic functional zeolite $\text{CoFe}_2\text{O}_4@\text{ZSM-5-600}$ composite catalyst shows a high cyclohexanone conversion of $\sim 96\%$ after the reaction is sustained for 60 min (**Figure 5B**). The selectivity is 100 % to the dimethoxycyclohexane and the yield of dimethoxycyclohexane achieves 90 % after the reaction for 1 h. Various solid-acid catalysts have shown good activities in the acetalization of cyclohexanone with methanol, such as mesoporous silica, zeolites, and metal oxides.^[57-60] Here, the conversion of cyclohexanone on our catalyst is above 90 % after 1 h reaction at 50 °C, which is much better than that of the commercial ZSM-5 ($\sim 80\%$) at the same condition. In our catalysts, the CoFe_2O_4 nanocrystals do not occupy the micropores of ZSM-5 and are surrounded by the ZSM-5 frameworks. Thus, the encapsulation of magnetic CoFe_2O_4 nanocrystals does not impact the diffusion of molecules and catalytic performance of ZSM-5. Meanwhile, due to the unique magnetic property, the $\text{CoFe}_2\text{O}_4@\text{ZSM-5}$ composites can be easily separated by a magnet from the solution and exhibit an identical performance even after more than six cycles of usage (**Figure 5C**). More importantly, the structure and magnetic property are well retained during the catalyst regeneration process in terms of calcination in air (**Figure 5D and 5E**). In previous reports, the magnetic function of Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$ is not stable in air condition. They are easily oxidized into $\alpha\text{-Fe}_2\text{O}_3$, thus losing the magnetic function.^[61-64] Furthermore, single crystal structure is also more stable mechanically than the polycrystalline aggregates.^[12, 65] In our work, the CoFe_2O_4 nanocrystals possess a stable magnetic property due to their synthesis by the air calcination. And the structure is also stable

due to the single crystal feature, which is beneficial for the harsh requirement in the catalytic application.

3. Conclusions

In summary, we have for the first time demonstrated the stable magnetic CoFe_2O_4 nanocrystals mediation over the functional zeolite ZSM-5 crystallization. The high relative crystallinity of CoFe_2O_4 nanocrystals with chemically stability, high mechanical hardness and superparamagnetic property results in a successful encapsulation into the single crystals of ZSM-5 to obtain magnetic functional zeolites due to non-further-grown nanocrystals during the fast ZSM-5 crystal growth. On the contrary, the CoFe_2O_4 nanocrystals with a low relative crystallinity and coercivity lead the polycrystalline zeolite growth to form microspheres composed of the assembled ZSM-5 nanorods and well-dispersed CoFe_2O_4 at the voids between the zeolite crystals due to the secondary growth of nanocrystals and large lattice mismatch between them. The successful encapsulation of small CoFe_2O_4 nanocrystals (~ 4 nm) into the ZSM-5 zeolite matrix lies on the pre-attachment of high crystalline nanocrystals on the pore surface of solid silica gel precursors. During the growth of ZSM-5 zeolite crystals, no secondary growth of nanocrystals happens and its motion is restricted. The magnetic functional zeolite $\text{CoFe}_2\text{O}_4@\text{ZSM-5-600}$ composite catalyst exhibits an excellent conversion and selectivity in the acetalization of cyclohexanone with methanol. Most importantly, the catalytic performance is not impacted by the encapsulation of magnetic CoFe_2O_4 nanocrystals. The presented design principles for functional zeolites may be applicable to magnetically stabilized beds which address high needs for catalysts with a superparamagnetic property and magnetic stability.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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References

- [1] J. J. De Yoreo, P. U. P. A. Gilbert, N. A. J. M. Sommerdijk, R. L. Penn, S. Whitlam, D. Joester, H. Zhang, J. D. Rimer, A. Navrotsky, J. F. Banfield, A. F. Wallace, F. M. Michel, F. C. Meldrum, H. Colfen, P. M. Dove, *Science* **2015**, 349, 6760.
- [2] G. Feng, P. Cheng, W. Yan, M. Boronat, X. Li, J.-H. Su, J. Wang, Y. Li, A. Corma, R. Xu, J. Yu, *Science* **2016**, 351, 1188.
- [3] C. Chen, Y. Kang, Z. Huo, Z. Zhu, W. Huang, H. L. Xin, J. D. Snyder, D. Li, J. A. Herron, M. Mavrikakis, M. Chi, K. L. More, Y. Li, N. M. Markovic, G. A. Somorjai, P. Yang, V. R. Stamenkovic, *Science* **2014**, 343, 1339.
- [4] D. Gu, W. Schmidt, C. M. Pichler, H. J. Bongard, B. Spliethoff, S. Asahina, Z. Cao, O. Terasaki, F. Schüth, *Angew. Chem. Int. Ed.* **2017**, 56, 11222.
- [5] G. Lu, S. Li, Z. Guo, O. K. Farha, B. G. Hauser, X. Qi, Y. Wang, X. Wang, S. Han, X. Liu, J. S. DuChene, H. Zhang, Q. Zhang, X. Chen, J. Ma, S. C. J. Loo, W. D. Wei, Y. Yang, J. T. Hupp, F. Huo, *Nat. Chem.* **2012**, 4, 310.
- [6] M. N. O'Brien, M. R. Jones, B. Lee, C. A. Mirkin, *Nat. Mater.* **2015**, 14, 833.

- [7] J.-D. Xiao, L. Han, J. Luo, S.-H. Yu, H.-L. Jiang, *Angew. Chem. Int. Ed.* **2018**, 57, 1103.
- [8] X. Fang, Q. Shang, Y. Wang, L. Jiao, T. Yao, Y. Li, Q. Zhang, Y. Luo, H.-L. Jiang, *Adv. Mater.* **2018**, 30, 1705112.
- [9] G. Chen, Y. Zhao, G. Fu, P. N. Duchesne, L. Gu, Y. Zheng, X. Weng, M. Chen, P. Zhang, C.-W. Pao, J.-F. Lee, N. Zheng, *Science* **2014**, 344, 495.
- [10] H. Zhang, Q. Xiao, X. Guo, N. Li, P. Kumar, N. Rangnekar, M. Y. Jeon, S. Al-Thabaiti, K. Narasimharao, S. N. Basahel, B. Topuz, F. J. Onorato, C. W. Macosko, K. A. Mkhoyan, M. Tsapatsis, *Angew. Chem.* **2016**, 128, 7300.
- [11] B. M. Weckhuysen, J. Yu, *Chem. Soc. Rev.* **2015**, 44, 7022.
- [12] B. Li, B. Sun, X. Qian, W. Li, Z. Wu, Z. Sun, M. Qiao, M. Duke, D. Zhao, *J. Am. Chem. Soc.* **2013**, 135, 1181.
- [13] M. Shete, M. Kumar, D. Kim, N. Rangnekar, D. Xu, B. Topuz, K. V. Agrawal, E. Karapetrova, B. Stottrup, S. Al-Thabaiti, S. Basahel, K. Narasimharao, J. D. Rimer, M. Tsapatsis, *Angew. Chem. Int. Ed.* **2017**, 56, 535.
- [14] B. Li, Z. Hu, B. Kong, J. Wang, W. Li, Z. Sun, X. Qian, Y. Yang, W. Shen, H. Xu, D. Zhao, *Chem. Sci.* **2014**, 5, 1565.
- [15] X. Shen, J. Kang, W. Niu, M. Wang, Q. Zhang, Y. Wang, *Catal. Sci. Technol.* **2017**, 7, 3598.
- [16] H. Li, Y. Wang, F. Meng, F. Gao, C. Sun, C. Fan, X. Wang, S. Wang, *RSC Adv.* **2017**, 7, 25605.
- [17] M. M. Rahman, B. M. Abu-Zied, M. M. Hasan, A. M. Asiri, M. A. Hasnat, *RSC Adv.* **2016**, 6, 48435.
- [18] K. A. Tarach, J. Tekla, W. Makowski, U. Filek, K. Mlekodaj, V. Girman, M. Choi, K. Gora-Marek, *Catal. Sci. Technol.* **2016**, 6, 3568.

- [19] C. Wang, L. Wang, J. Zhang, H. Wang, J. P. Lewis, F.-S. Xiao, *J. Am. Chem. Soc.* **2016**, 138, 7880.
- [20] J. Mielby, J. O. Abildstrøm, F. Wang, T. Kasama, C. Weidenthaler, S. Kegnaes, *Angew. Chem. Int. Ed.* **2014**, 53, 12513.
- [21] S. Goel, S. I. Zones, E. Iglesia, *J. Am. Chem. Soc.* **2014**, 136, 15280.
- [22] A. B. Laursen, K. T. Højholt, L. F. Lundegaard, S. B. Simonsen, S. Helveg, F. Schüth, M. Paul, J.-D. Grunwaldt, S. Kegnaes, C. H. Christensen, K. Egeblad, *Angew. Chem. Int. Ed.* **2010**, 49, 3504.
- [23] M. Rahman, B. M. Abu-Zied, A. M. Asiri, *RSC Adv.* **2017**, 7, 21164.
- [24] M. M. Rahman, B. M. Abu-Zied, A. M. Asiri, *J. Ind. Eng. Chem.* **2018**, 61, 304.
- [25] X. Qian, D. Xiong, A. M. Asiri, S. B. Khan, M. M. Rahman, H. Xu, D. Zhao, *J. Mater. Chem. A* **2013**, 1, 7525.
- [26] Z. Song, Q. Zhang, P. Ning, Y. Wang, Y. Duan, J. Wang, Z. Huang, *RSC Adv.* **2016**, 6, 111389.
- [27] T.-L. Cui, W.-Y. Ke, W.-B. Zhang, H.-H. Wang, X.-H. Li, J.-S. Chen, *Angew. Chem. Int. Ed.* **2016**, 55, 9178.
- [28] N. Wang, Q. Sun, R. Bai, X. Li, G. Guo, J. Yu, *J. Am. Chem. Soc.* **2016**, 138, 7484.
- [29] A. Sathya, P. Guardia, R. Brescia, N. Silvestri, G. Pugliese, S. Nitti, L. Manna, T. Pellegrino, *Chem. Mater.* **2016**, 28, 1769.
- [30] C. Velez, I. Torres-Díaz, L. Maldonado-Camargo, C. Rinaldi, D. P. Arnold, *ACS Nano* **2015**, 9, 10165.
- [31] A. Rumplecker, F. Kleitz, E.-L. Salabas, F. Schüth, *Chem. Mater.* **2007**, 19, 485.
- [32] C. A. Chagas, E. F. de Souza, M. C. N. A. de Carvalho, R. L. Martins, M. Schmal, *Appl. Catal. A: Gen.* **2016**, 519, 139.
- [33] B. Cai, M. Zhao, Y. Ma, Z. Ye, J. Huang, *ACS Appl. Mater. Interfaces* **2015**, 7, 1327.

- [34] Q. Yang, H. Choi, S. R. Al-Abed, D. D. Dionysiou, *Appl. Catal.B: Environ.* **2009**, 88, 462.
- [35] K. Klaigaew, C. Samart, C. Chaiya, Y. Yoneyama, N. Tsubaki, P. Reubroycharoen, *Chem. Eng. J.* **2015**, 278, 166.
- [36] R. Shankar, K. Senthilkumar, P. Kolandaivel, *Int. J. Quantum Chem.* **2009**, 109, 764.
- [37] Y. El Mendili, J.-F. o. Bardeau, N. Randrianantoandro, F. Grasset, J.-M. Greneche, *J. Phys. Chem. C* **2012**, 116, 23785.
- [38] J. Zhang, Y. Tang, K. Lee, M. Ouyang, *Science* **2010**, 327, 1634.
- [39] J.-S. Lee, E. V. Shevchenko, D. V. Talapin, *J. Am. Chem. Soc.* **2008**, 130, 9673.
- [40] C. Wang, C. Xu, H. Zeng, S. Sun, *Adv. Mater.* **2009**, 21, 3045.
- [41] M. Choi, Z. Wu, E. Iglesia, *J. Am. Chem. Soc.* **2010**, 132, 9129.
- [42] W. Zhou, *Adv. Mater.* **2010**, 22, 3086.
- [43] F. M. Michel, V. Barrón, J. Torrent, M. P. Morales, C. J. Serna, J.-F. Boily, Q. Liu, A. Ambrosini, A. C. Cismasu, G. E. Brown, *Proc. Natl. Acad. Sci.* **2010**, 107, 2787.
- [44] D. Li, F. Soberanis, J. Fu, W. Hou, J. Wu, D. Kisailus, *Cryst. Growth Des.* **2013**, 13, 422.
- [45] R. Das, J. Alonso, Z. Nematiporshokouh, V. Kalappattil, D. Torres, M.-H. Phan, E. Garaio, J. Á. García, J. L. Sanchez Llamazares, H. Srikanth, *J. Phys. Chem. C* **2016**, 120, 10086.
- [46] H. Khurshid, W. Li, S. Chandra, M.-H. Phan, G. C. Hadjipanayis, P. Mukherjee, H. Srikanth, *Nanoscale* **2013**, 5, 7942.
- [47] V. Lopez-Dominguez, J. M. Hernández, J. Tejada, R. F. Ziolo, *Chem. Mater.* **2013**, 25, 6.
- [48] S. Alam, C. Anand, K. Ariga, T. Mori, A. Vinu, *Angew. Chem. Int. Ed.* **2009**, 48, 7358.
- [49] D. Erdem, N. S. Bingham, F. J. Heiligt, N. Pilet, P. Warnicke, L. J. Heyderman, M. Niederberger, *Adv. Funct. Mater.* **2016**, 26, 1954.

- [50] S. Permien, S. Indris, G. Neubüser, A. Fiedler, L. Kienle, S. Zander, S. Doyle, B. Richter, W. Bensch, *Chem. Eur. J.* **2016**, 22, 16929.
- [51] D. Peddis, C. Cannas, A. Musinu, A. Ardu, F. Orrù, D. Fiorani, S. Laureti, D. Rinaldi, G. Muscas, G. Concas, G. Piccaluga, *Chem. Mater.* **2013**, 25, 2005.
- [52] L. H. Reddy, J. L. Arias, J. Nicolas, P. Couvreur, *Chem. Rev.* **2012**, 112, 5818.
- [53] B. Liu, Q. Li, B. Zhang, Y. Cui, H. Chen, G. Chen, D. Tang, *Nanoscale* **2011**, 3, 2220.
- [54] C. Cannas, A. Musinu, A. Ardu, F. Orrù, D. Peddis, M. Casu, R. Sanna, F. Angius, G. Diaz, G. Piccaluga, *Chem. Mater.* **2010**, 22, 3353.
- [55] Q. Song, Z. J. Zhang, *J. Am. Chem. Soc.* **2012**, 134, 10182.
- [56] T. Yamanaka, A. Kondoh, M. Terada, *J. Am. Chem. Soc.* **2015**, 137, 1048.
- [57] A. Sinhamahapatra, N. Sutradhar, M. Ghosh, H. C. Bajaj, A. B. Panda, *Appl. Catal. A: Gen.* **2011**, 402, 87.
- [58] M. Iwamoto, Y. Tanaka, N. Sawamura, S. Namba, *J. Am. Chem. Soc.* **2003**, 125, 13032.
- [59] A. S. Poyraz, C.-H. Kuo, E. Kim, Y. Meng, M. S. Seraji, S. L. Suib, *Chem. Mater.* **2014**, 26, 2803.
- [60] J.-Y. Liu, J.-G. Wang, N. Li, H. Zhao, H.-J. Zhou, P.-C. Sun, T.-H. Chen, *Langmuir* **2012**, 28, 8600.
- [61] D. Jie, X. Zhenghe, M. K. Steven, *Adv. Funct. Mater.* **2009**, 19, 1268.
- [62] A. B. Bourlinos, R. Zboril, D. Petridis, *Microporous Mesoporous Mater.* **2003**, 58, 155.
- [63] F. Jiao, J.-C. Jumas, M. Womes, A. V. Chadwick, A. Harrison, P. G. Bruce, *J. Am. Chem. Soc.* **2006**, 128, 12905.
- [64] E. R. Monazam, R. W. Breault, R. Siriwardane, *Ind. Eng. Chem. Res.* **2014**, 53, 13320.
- [65] Y. Deng, C. Deng, D. Qi, C. Liu, J. Liu, X. Zhang, D. Zhao, *Adv. Mater.* **2009**, 21, 1377.

Figure 1. Scheme of ZSM-5 crystallization mediated by attached CoFe₂O₄ nanocrystals with different relative crystallinity

Figure 2. SEM (a, b, c), TEM images (d, e, f) and CoFe₂O₄-based particle size distributions (g, h, i) of the obtained CoFe₂O₄@ZSM-5-600, CoFe₂O₄@ZSM-5-400 and CoFe₂O₄@ZSM-5-200 composites (Inset in d: SAED pattern, scale bar: 5 1/nm).

Figure 3. (A) The relative crystallinity functioned with the calcination temperature of the CoFe₂O₄ nanocrystals attached in the mesoporous silica gel; (B) XRD patterns, (C) TPR profiles of CoFe₂O₄@SiO₂ calcined at different temperature: (a) 200, (b) 400, (c) 600 °C.

Figure 4. Hysteresis loops recorded at 300 K (A) and 5 K (B) of the samples CoFe₂O₄@ZSM-5-200 (a), CoFe₂O₄@ZSM-5-400 (b), CoFe₂O₄@ZSM-5-600 (c) composites; ZFC and FC curves of CoFe₂O₄@ZSM-5-600 (C) and pure CoFe₂O₄ nanocrystals (D) prepared through adding NaOH solution into iron and cobalt ion aqueous solution.

Figure 5. (A) The scheme for the acetalization of cyclohexanone with methanol; (B) the conversion of cyclohexanone functioned with reaction time; (C) the reusability measurement of $\text{CoFe}_2\text{O}_4@\text{ZSM-5-600}$ catalysts; (D) the XRD patterns and (E) hysteresis loops recorded at 300 K of the $\text{CoFe}_2\text{O}_4@\text{ZSM-5-600}$ before and after catalytic evaluation.

Guest CoFe_2O_4 nanocrystals with different relative crystallinity lead to different host ZSM-5 crystallization behaviour. Nanocrystals with high crystallinity leads to a successful encapsulation into the zeolite single crystal. Low crystallinity nanocrystals composed of ions, amorphous and crystalline result to polycrystalline ZSM-5 growth.

nanocrystals, crystallization, zeolite, functionalization, catalysis

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CoFe_2O_4 Nanocrystals Mediated Crystallization Strategy for Magnetic Functioned ZSM-5 Catalysts