Stabilization of nanosized MgFe_2O_4 nanoparticles in phenylene-bridged KIT-6-type ordered mesoporous organosilica (PMO)

Jana Timm^{a,**}, André Blöcher^a, Siyuan Zhang^b, Christina Scheu^b, Roland Marschall^{a,*}

^a Chair of Physical Chemistry III, University of Bayreuth, Universitätsstrasse 30, 95447, Bayreuth, Germany

^b Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str. 1, 40237, Düsseldorf, Germany

ABSTRACT

The unique combination of two functional materials, namely the earth-abundant spinel magnesioferrite (MgFe_2O_4) and mesoporous phenylene-bridged KIT-6-type organosilica, was developed. The mesoporous organosilica acts as host matrix for the nanosized MgFe_2O_4 particles which leads to better dispersibility and increased stability towards acids. Additionally, the mesoporous host is a very good material to generate a toolbox towards applicable materials due to flexible functionalization. Nanosized, monodisperse MgFe_2O_4 crystallites were synthesized *via* a facile microwave assisted non-aqueous reaction path. Afterwards, the particles were embedded in phenylene-bridged periodic mesoporous organosilica with 3D cubic pore arrangement (KIT-6-type PMO) generating a new kind of mesoporous inorganic-organic hybrid material ($\text{MgFe}_2\text{O}_4@\text{phe-PMO}$). The $\text{MgFe}_2\text{O}_4@\text{phe-PMO}$ exhibits the characteristics of both components: A high specific surface area of $1164 \text{ m}^2\text{g}^{-1}$ with clearly defined and highly ordered micro- and mesopores (1.5 and 6.8 nm), and the broad absorption of visible and UV light due to the phenylene bridging units in the PMO and the MgFe_2O_4 particles. The presence of MgFe_2O_4 nanoparticles in the PMO matrix is proven by UV/Vis spectroscopy, powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM). Selected area electron diffraction (SAED) and Scanning TEM in atomic resolution was chosen to demonstrate the crystallinity and phase purity of MgFe_2O_4 particles in the hybrid material. An additional focus was laid on calcination of the $\text{MgFe}_2\text{O}_4/\text{PMO}$ hybrids to remove template molecules, while preventing rearrangement or shrinkage of the pore system and to promote further crystallization of the MgFe_2O_4 nanoparticles.

1. Introduction

Since the first appearance of ordered mesoporous silica (OMS) materials in 1992 [1], research in this area increased tremendously due to the unique characteristics of this class of materials including high specific surface areas of about $1000 \text{ m}^2\text{g}^{-1}$ and narrow pore size distributions. The pore ordering and size can be tuned by simply adjusting the reaction parameters [2–6]. Additionally, OMS are resistant against most of the commonly used chemicals, and their surfaces can easily be functionalized by three different methods [7,8].

Using post-synthetic grafting methods, OMS are synthesized at first followed by (organo)alkoxysilane molecules being anchored on the surface of the OMS by condensation [7,9]. The grafting method is suitable for many (organo)alkoxysilanes, but the degree of functionalization in OMS is limited by the amount of silanol groups on the surface of OMS.

The second functionalization method is the so-called co-condensation, in which (organo)alkoxysilane molecules react with alkoxysilanes like tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) while forming OMS network with embedded functional groups derived from (organo)alkoxysilanes. This method leads to higher functionalization degrees, but is also limited by the suitable ratio of TEOS/TMOS to (organo)alkoxysilane [10–13].

The third method is the formation of periodic mesoporous organosilica (PMO). In this reaction only organic (bis)silylated precursor molecules were used to get highly ordered porous networks. The synthesis of PMOs is very sensitive to reaction parameter changes, just like OMS syntheses in general [14–18]. PMOs exhibit all characteristics mentioned for OMS like narrow pore size distribution, high specific surface areas, and tunable pore arrangements. The main advantage of PMOs vs. OMS is the integration of organic functional groups in amounts which are not achievable by any other functionalization

* Corresponding author.

** Corresponding author.

E-mail addresses: jana.timm@uni-bayreuth.de (J. Timm); roland.marschall@uni-bayreuth.de (R. Marschall)

method. The degree of organic functional groups reaches 100%. PMOs are not functionality-limited, so the PMO material could be tailored for the desired application. Therefore, PMOs with more or less hydrophilic surface areas or heteroatom containing ones are possible [19–25]. PMOs also have a high chemical stability comparable to OMS. This chemical stability makes them suitable as host materials for substances which are less chemically stable under specific conditions e.g. in acidic or alkaline solutions, like some iron oxides are unstable under acidic conditions [26].

Iron oxides and especially spinel ferrites [27] have drawn a lot of attention during the last few years due to several reasons. Many of them consist of earth-abundant elements, have low toxicity, and variable applicability [28,29]. Furthermore, the materials exhibit outstanding characteristics for medical [30], magnetic [30–32], energy storage and photocatalytic [33,34] applications. The widely used ferrites with the general composition of AFe_2O_4 ($A = Zn^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, \dots$) can be synthesized as nanoparticles (NPs) to improve performance in the mentioned applications. Several studies also show improvements on the magnetic field strength [28,31,32,35].

The improvement of magnetic behavior of the ferritic NPs is unfortunately a huge problem regarding technical usage of the NPs for instance in heterogeneous catalysis. The particles are influenced by magnetic devices like stirring equipment which can lead to segregation and consequently non-homogeneous distribution of the catalyst in the reaction medium [31,36–38]. Hence, the development of stabilization strategies against undesired magnetic interaction like precipitation on the vessel bottom is important to make ferrite NPs suitable for catalytic application and to achieve in general stable dispersion for several applications. Another huge problem besides the magnetic behavior is the low chemical stability of ferritic NPs in acidic solutions [26,39]. A third reason for stabilization of ferritic NPs in solution is to minimize the risk of dust exposure while handling and processing.

The stabilization of ferrite NPs in dispersion is possible after or during synthesis [31,35,40,41]. A lot of synthesis strategies for ferrite NPs and the further preparation of stable ferrite NP dispersions are known like sol-gel [42,43] or solvothermal [44–46], high temperature [47,48], mechanochemical routes [49], or microwave-assisted procedures [50,51]. Recently, we could show that stable $MgFe_2O_4$ NP dispersions could be achieved by employment of appropriate capping agents in aqueous and also non-aqueous solvents [51]. Suitable capping agents for the stabilization are PVP (Polyvinylpyrrolidone), TOPO (Trioctylphosphine oxide), Oleylamine etc. [47,48,52–56] Another method to stabilize ferritic NPs in solution is the formation of core-shell systems, where NPs (core) are surrounded by stabilizing shells (silica, etc.) [57–60]. To utilize the catalytic/surface properties of the ferrite NP core, the shell has to be porous to allow the transport of reagents to the ferritic NP core. In some cases the pores could be tailored allowing only the right reactant to reach the catalytically active surface [61–65]. However those particles could still be magnetic, being problematic in heterogeneous catalysis and the ferritic part/core of the particle is still unstable in acidic media.

Therefore, we focused on the embedment of particles in a mesoporous PMO matrix to make the material less magnetic [66] and to enhance the stability in dispersion as well as against acidic solutions. Thus, a unique functional, mesoporous material could be created. The combination of $MgFe_2O_4$ NPs and 3D cubic phenylene-bridged PMO ($MgFe_2O_4@phe-PMO$) is synthetically demanding, novel, and very promising regarding (photo-)catalytic applications, where stabilized $MgFe_2O_4$ NPs are needed and the mesoporous characteristics of the phenylene-bridged PMO (phe-PMO) shall be exploited. This strategy could be easily expanded to other comparable ferrite materials in the future, like $NiFe_2O_4$, $CoFe_2O_4$ or Fe_3O_4 .

2. Experimental section

2.1. Chemicals

1,4-Bis(triethoxysilyl)benzene (BTEB, 96%, Sigma-Aldrich), Pluronic P123® (Sigma-Aldrich), *rac*-1-phenylethanol (98%, Sigma-Aldrich); 1-butanol (Grüssing, 99%, puriss.); hydrochloric acid (Julius Hoesch, 36–38%, purum); ethanol (VWR, >99%) magnesium acetylacetonate ($Mg(acac)_2$, 98%, TCI), iron (III)acetylacetonate ($Fe(acac)_3$, >99%, Acros Organics), *n*-pentane (Stockmeier, technical grade), diethylether (VWR, >99%). All reagents were used without further purification.

2.2. Synthesis

We choose the phenylene-bridged PMO with 3D cubic pore arrangements as stabilization matrix for the $MgFe_2O_4$ NPs. Our synthetic co-condensation approach is presented compared to the classical synthesis of phenylene-bridged PMO approach in Scheme 1.

For synthesis of $MgFe_2O_4$ nanoparticles a known microwave synthesis method was modified here [51]. 194.7 mg (0.875 mmol) of magnesium acetylacetonate were dissolved in 15 mL *rac*-1-phenylethanol using an ultrasonic bath. Then 353.2 mg (1 mmol) of iron(III) acetylacetonate were added and dissolved. The solution was transferred into a 30 mL borosilicate microwave vial and heated to 250 °C in the microwave for 30 min under continuous stirring (300 rpm). The obtained particles were precipitated in *n*-pentane, and washed three times with demineralized water and once with diethylether. After drying overnight under vacuum at room temperature, the particles were obtained as a brown powder which was calcined at 500 °C for 1 h (heating ramp: 10 °C min⁻¹) to remove organic residues and induce crystallization of the material.

Synthesis of the phenylene-bridged PMO with 3D cubic pore structure (KIT-6 analogue) was executed analogue to the synthesis of Ryoo et al. [15].

In a typical synthesis of the hybrid material, $MgFe_2O_4@phe-PMO$, 1.46 g Pluronic P123® were dissolved in a mixture of 2.8 mL 2 M HCl and 40 mL H₂O at 40 °C overnight. Afterwards, 1.4 mL 1-butanol (15.3 mmol) were added and the solution was stirred for 1 h. Subsequently, 1 mL 1,4-Bis(triethoxysilyl)benzene (BTEB) (2.5 mmol) was added. During this step the originally clear solution turns opaque due to the formation of PMO particles. 24 h later, the colourless dispersion was transferred to a Teflon beaker. After addition of 56.0 mg of freshly ground $MgFe_2O_4$ NPs, the dispersion in the Teflon beaker was carefully stirred (with a glass rod for 1 min), put in a steel autoclave, and the gel was aged at 100 °C for 72 h. Then the dispersion was cooled down, the solid was filtered off and washed three times with ethanol and water.

For calcination, the yellowish powder was heated to 400 °C with a heating ramp of 6.66 °C min⁻¹. The holding time at 400 °C was 3 h. Afterwards the furnace was cooled down with a cooling rate of 11.66 °C min⁻¹ to 50 °C and then cooled down to room temperature (cooling rate: 3 °C min⁻¹).

For comparison, Soxhlet extraction was carried out for removal of the template. The yellowish powder was therefore transferred to extraction shucks and extracted overnight (approx. 16 h) with a solution of 1000 mL ethanol and 31 mL conc. HCl (pH value ≈ 1). Afterwards, the solid was dried at 80 °C overnight.

2.3. Equipment

For microwave-assisted synthesis, a *Monowave 400* ($f = 2.45$ GHz, Anton Paar Germany GmbH) equipped with a hydraulic pressure and

Scheme 1. top: Classical synthesis of phenylene bridged KIT-6 PMO; bottom: our synthetic approach to embed ferritic NPs in the PMO matrix via co-condensation.

IR temperature sensor was used. All reaction solutions were magnetically stirred at 300rpm during microwave heating.

Optical properties of the materials were measured in diffuse reflectance collected from 800 nm to 200 nm with step width of 1 nm on a PerkinElmer *Lambda 750* UV/Vis-NIR-spectrometer equipped with a PrayingMantis mirror arrangement. Reflection spectra were converted into absorption spectra via Kubelka-Munk formula.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were collected using a Bruker alpha with interchangeable measurement modules.

Raman spectroscopy was performed using a Senterra Raman spectrometer (Bruker) with a Nd:YAG laser ($\lambda_{\text{ex}} = 532$ nm). The powder samples were spread on a microscope slide and placed under the microscope.

Nitrogen physisorption measurements were performed using a Quantachrome Autosorb iQ. The nitrogen physisorption isotherms were collected at 77 K after degassing the samples for 24 h at 120°C .

Thermogravimetric analysis was performed on a STA409PC thermoscale (Netzsch) with a QMG421 quadrupole mass spectrometer (MS) from Balzers (heating rate of 5 K/min, synthetic air 80:20 = $\text{N}_2:\text{O}_2$, temperature range 32°C – 1000°C).

Powder X-ray diffraction (PXRD) data was collected using a PANalytical Empyrean diffractometer equipped with a *PIXcel3D* detector using CuK_α radiation (emission current = 40 mA, acceleration voltage = 40 kV).

For *Transmission electron microscopy (TEM)* the sample powder was suspended in ethanol and dropped on carbon sputtered copper grids (Plano GmbH). Prepared and dried samples were analyzed in a Philips CM 30-ST electron microscope equipped with a LaB_6 cathode (300 kV). Scanning TEM (STEM) investigation was conducted using a Titan Themis microscope operated at 300 kV. Aberration correction allows for a STEM probe size of $< 1 \text{ \AA}$ (semi-convergence angle of 24 mrad). High angle annular dark field (HAADF) micrographs were collected using scattered electrons between 73 and 200 mrad . Energy dispersive X-ray spectroscopy (EDS) spectrum imaging was acquired using the Super-X system with four silicon drift detectors. Multivariate analysis was

applied to reduce the statistical noise and identify the main spectral features [73].

Synchrotron experiments were performed at P02.1, Deutsches Elektronen-Synchrotron, Hamburg (DESY). Sample powder was measured in a sealed quartz capillary and at fixed energy of 60 keV. The diffractometer was equipped with a fast area detector XRD1621 (PerkinElmer).

3. Results and discussion

The materials synthesized according to Scheme 1 (Experimental Section) were assigned as $\text{assyn-MgFe}_2\text{O}_4@\text{phe-PMO}$ for the as-synthesized sample and $\text{calc-MgFe}_2\text{O}_4@\text{phe-PMO}$ for the calcined sample in the following.

The embedment of the MgFe_2O_4 NPs in the phenylene-bridged PMO (phe-PMO) could be investigated by XRPD measurements. Therefore, the X-ray diffraction patterns of assyn- and $\text{calc-MgFe}_2\text{O}_4@\text{phe-PMO}$ samples are presented in Fig. 1. In the small angle X-ray diffraction (SAXRD) pattern of the assyn sample, signals at 0.97° ($d_{211} = 9.104 \text{ nm}$) and 1.11° ($d_{220} = 7.955 \text{ nm}$) 2θ arise indicating the presence of highly ordered 3D cubic pore arrangement. The SAXRD pattern of the calcined sample exhibits also two signals at 1.00° ($d_{211} = 8.83 \text{ nm}$) and 1.11° ($d_{220} = 7.746 \text{ nm}$) 2θ . The according signal positions of assyn- and $\text{calc-MgFe}_2\text{O}_4@\text{phe-PMO}$ fit very well to each other and also to the literature values of phenylene-bridged PMO materials with 3D cubic pore structures ($1a\bar{3}d$) [15]. This observation shows that our optimized calcination procedure is not inducing any structural transformation of the 3D cubic PMO walls during template removal, only generating the desired 3D cubic pore structure with nearly identical lattice parameter.

To find the optimum conditions, different calcination procedures were tested. One experiment resulted in a PMO material (calc-sh) with a shrunken pore system, which could be proven by the shift of 211 reflection in SAXRD pattern (Fig. S1 in the Supporting Information SI). The holding time was varied, as $\text{calc-sh MgFe}_2\text{O}_4@\text{phe-PMO}$ was calcined for 20 h, while $\text{calc-MgFe}_2\text{O}_4@\text{phe-PMO}$ was only calcined for 3 h. The calcination temperature of 400°C was chosen due to thermogravimetric analysis, in which we observed the complete template removal was already been achieved at 400°C (TG-MS, Fig. S2 in SI). The

Fig. 1. PXRD patterns of assyn-MgFe₂O₄@phe-PMO (a) and calc-MgFe₂O₄@phe-PMO (b). The small angle region is presented in the front, while the insets present the wide angle region.

calcination temperature has no impact on the embedded MgFe₂O₄ NPs, because the NPs were calcined at 500 °C before integration into the PMO network (see experimental section). The complete removal of the template molecules was also confirmed by DRIFT spectroscopy and the results will be discussed in detail later on.

The wide angle X-ray diffraction (WAXRD) patterns of assyn- and calc-MgFe₂O₄@phe-PMO show several reflections (Fig. 1), the broad reflections at 11.14° (assyn, $d = 0.794$ nm) and 10.71° (calc, $d = 0.827$ nm) 2θ can be assigned to the ordered phenylene rings in the pore walls (only low ordering). This phenomenon was observed earlier and the values are in good agreement with literature [14,15]. The reflections at 22.98° (assyn) and 23.80° (calc) 2θ originate from amorphous condensed silica [67,68]. Additionally, reflections with lower intensity are visible in the range from 30 to 70° 2θ . These reflections can be assigned to MgFe₂O₄ NPs (JCPDS 036-0398) and match completely to the reflections of pure, calcined MgFe₂O₄ NPs (Fig. S3 in SI) [51]. The results of WAXRD demonstrate the combination of phe-PMO and MgFe₂O₄ NPs in one material.

Due to difficult identification of MgFe₂O₄ NPs in the phe-PMO by WAXRD (only reflections with low intensity), transmission electron microscopy (TEM) images and corresponding selected area electron diffraction (SAED) patterns were collected.

The TEM image of calc-MgFe₂O₄@phe-PMO (Fig. 2a) shows a morphology which suggests a highly ordered pore structure of the PMO material. The observed morphology is comparable to those known from

literature [69–71]. After calcination the SAED pattern shows defined spots from segregated MgFe₂O₄ NPs (Fig. 2b) [51]. Well defined diffraction rings are visible and clearly indicate the presence of crystalline MgFe₂O₄ species. The most intense diffraction ring in the SAED pattern of calc-MgFe₂O₄@phe-PMO is the (111) reflection.

HAADF-STEM micrographs reveal more details on the structure of the calc-MgFe₂O₄@phe-PMO. The iron in MgFe₂O₄ has a higher atomic number and the NPs hence appear brighter than the surrounding phe-PMO matrix. In Fig. 3a the rough surface structure of the hybrid materials is visible and comparable to Fig. 2b and the literature [72]. Atomic resolution imaging (Fig. 3c) confirms individual NPs have the spinel structure and good crystallinity.

Further STEM images (Fig. 4 a-c) show the segregation of the NPs, while forming small agglomerates especially on the edges of the PMO with sizes around 20–30 nm. The formation of such small agglomerates is expected due to the fact that the NPs are not perfectly homogenous dispersed in the solution, while forming the PMO network around them (cf. Scheme 1). The size of these agglomerates is acceptable and is still in the area of few nanometres.

The two phases MgFe₂O₄ and phe-PMO are readily separated by their EDS spectra using multivariate analysis [73]. As shown in Fig. 5, the NPs (phase 2) show the Fe-L, Mg-K, Fe-K peaks and they are embedded in the PMO matrix (phase 1), which has a higher Si-K peak. There is no indication of chemical segregation at the NPs, which corresponds well to the good crystallinity of the spinel phase (Fig. 4c).

Fig. 2. TEM image of calc-MgFe₂O₄@phe-PMO (a); related SAED of calc-MgFe₂O₄@phe-PMO with discrete intensities corresponding to MgFe₂O₄ reflections (b).

Fig. 3. STEM images of calc-MgFe₂O₄@phe-PMO at different magnifications (a,b) up to the atomic scale and inset of the crystal structure of MgFe₂O₄ spinel with space group Fd $\bar{3}$ m, viewed along [11-2] zone axis (c).

Fig. 4. STEM images of calc-MgFe₂O₄@phe-PMO at different magnifications. The images show clearly the formation of small NPs agglomerates.

The integration of MgFe₂O₄ NPs is proven by XRD, TEM, SAED, STEM and EDS mapping. To define the pore systems regarding pore ordering (in addition to SAXRD) and to determine pore size and specific surface area, nitrogen physisorption measurements were performed. The nitrogen physisorption isotherm of calc-MgFe₂O₄@phe-PMO de-

scribes the typical behaviour of mesoporous materials (IUPAC classification [74]: IVa isotherm, Fig. 6a). Calc-MgFe₂O₄@phe-PMO exhibits a high specific surface area of about 1164 m²g⁻¹ (BET method). The values are slightly higher than the literature values of about 927 m²g⁻¹ [15].

The pore size distribution (NLDFT analysis, Fig. 6b) displays two maxima indicating micropores of 1.5 nm and mainly mesopores of 6.8 nm. The micropores connect the mesopores, which is comparable to OMS like SBA-15 or KIT-6. More importantly, the narrow pore size distribution demonstrates that the integration of MgFe₂O₄ NPs has no impact on the pore ordering.

Calc-MgFe₂O₄@phe-PMO exhibits high specific surface area and a highly ordered pore system with clearly defined mesopores. The aforementioned complete removal of the template molecules could also be proven by DRIFT spectroscopy. Additionally, DRIFT spectra were measured to gain information about the general chemical nature of the

Fig. 5. STEM-EDS spectrum imaging of calc-MgFe₂O₄@phe-PMO (a) from the area indicated by the box. Two phases are identified by (b) their EDS spectra. The spatial distribution of (c) phase 1 and (d) phase 2 corresponds to the PMO matrix and MgFe₂O₄ NPs, respectively.

Fig. 6. (a) Nitrogen physisorption isotherm of calc-MgFe₂O₄@phe-PMO; (b) pore size distribution of calc-MgFe₂O₄@phe-PMO (NLDFT method).

MgFe₂O₄@phe-PMO. In the DRIFT spectrum of assyn-MgFe₂O₄@phe-PMO (Fig. 7, black) the presence of Pluronic P123® template molecules is obvious due to the intense vibration bands at 2874–2935 and 2972 cm^{-1} and C-H stretching and bending vibrations in the range between 1500 and 1350 cm^{-1} [75–79]. The other vibration bands derived from the phe-PMO network [80,81] and the broad spectral feature around 3380 cm^{-1} are due to adsorbed water molecules on the surface. In the DRIFT spectrum of calc-MgFe₂O₄@phe-PMO (Fig. 7, blue) vibration bands of Pluronic P123® are missing, indicating successful and complete removal of template molecules. In the difference plot of assyn-MgFe₂O₄@phe-PMO vs. calc-MgFe₂O₄@phe-PMO (Fig. 7, red) the changes are even more prominent.

Another huge difference is noticeable at high wavenumbers, the band centred at 3380 cm^{-1} is less intense after the calcination and the maximum of the signal splits into two due to different types of hydrogen bonds between PMO network and adsorbed water [82–84]. The sharp, intense vibration band arising at 3639 cm^{-1} could be assigned to terminal isolated silanol groups on the surface [82,83,85]. In calc-MgFe₂O₄@phe-PMO, silanol groups are not interacting with the template molecules over hydrogen-bonding (already removed by calcination), and therefore isolated silanol groups exist in calc-MgFe₂O₄@phe-PMO [82]. In addition, all vibrations which originate from the phe-PMO network are still present [80]. Due to polar silanol groups on the surface and organic phenylene bridging units in the pore walls, calc-

MgFe₂O₄@phe-PMO is predestined to perform attractive interactions with organic (non-polar) and inorganic (polar) molecules or solvents simultaneously. In summary, the DRIFT spectra unfold the chemical nature of both organic-inorganic hybrid materials and show clearly the removal of template molecules by calcination.

The successful combination of these highly applicable materials MgFe₂O₄ NPs and phenylene-bridged PMO has one more very interesting feature. Both components can absorb light in different wavelength regions. The phe-PMO can absorb UV light [86] while MgFe₂O₄ NPs absorb visible light [51], resulting in broad light absorption of the hybrid material. This effect can be observed by UV/vis spectroscopy. In Fig. 8 the Kubelka-Munk absorption spectra (Fig. 8a) and Tauc plots (Fig. 8b) of phenylene-bridged PMO (phe-PMO), assyn- and calc-MgFe₂O₄@phe-PMO are shown. The intense absorption bands at 270 nm (4.6 eV) and 276 nm (4.5 eV) in absorption spectra and Tauc plots (Fig. 8) can be assigned to the aromatic phenylene bridges in the PMO network [14,86,87]. The spectra confirm that the hybrid materials contain phenylene bridge units. The extension of the absorption into the visible light range of assyn- and calc-MgFe₂O₄@phe-PMO indicates the presence of visible light absorbing species in the material. The indirect Tauc-plots of all three materials (phe-PMO, assyn-MgFe₂O₄@phe-PMO and calc-MgFe₂O₄@phe-PMO, Fig. 8b) make the changes in the light absorption behavior more clearly. No absorption of phe-PMO is observable below 4.0 eV, while assyn- and calc-MgFe₂O₄@phe-PMO absorb light up to 2 eV. The absorption in the visible range fits very well to the optical properties of MgFe₂O₄ NPs, which have a direct band gap of 2.4 eV [51] and absorb a large amount of visible light. MgFe₂O₄ NPs exhibit brownish color, while assyn- and calc-MgFe₂O₄@phe-PMO appear slightly yellow due to dilution of MgFe₂O₄ NPs in the PMO network (picture of assyn-MgFe₂O₄@phe-PMO in SI, Fig. S4 in SI). This optical observation of the materials fits very well to the UV/Vis spectroscopy results.

To test the resistance of the embedded MgFe₂O₄ NPs against acids and to test another common way to remove template molecules, Soxhlet extraction was performed. The solvent mixture is an acidic ethanol solution with a pH value around 1. During extraction, the powder gets in contact with the acidic solution and the template molecules were dissolved and washed out of the silica [7,16,22]. This Soxhlet extraction procedure might lead to leaching out of the ferritic species from the silica due to the low stability of MgFe₂O₄ NPs in acidic media [26,39]. In case of our assyn-MgFe₂O₄@phe-PMO the ferritic species is still present after Soxhlet extraction with acidic ethanolic solution (31 mL conc. HCl : 1000 mL ethanol). This stabilization effect of the PMO network and the ferritic NPs could be proven by PXRD using synchrotron radiation. The synchrotron PXRD pattern is presented in Fig. 9. The Soxhlet-extracted MgFe₂O₄@phe-PMO (extrac-MgFe₂O₄@phe-PMO) shows still all reflections of MgFe₂O₄ in the hybrid.

Fig. 7. DRIFT spectra of assyn- and calc-MgFe₂O₄@phe-PMO.

Fig. 8. a) Kubelka-Munk spectra of phe-PMO, assyn- and calc-MgFe₂O₄@phe-PMO; b) indirect Tauc plot of phe-PMO, assyn- and calc-MgFe₂O₄@phe-PMO samples.

Fig. 9. PXRD pattern measured with synchrotron radiation ($\lambda = 0.20722$ Å) compared to the calculated pattern of MgFe₂O₄.

The incorporation of MgFe₂O₄ NPs in the PMO material and the improved stability against acids/acidic solutions are impressively shown by these experiments. The drawback of the Soxhlet extraction is that the removal of template molecules does not proceed quantitatively (Raman and nitrogen physisorption data in the SI, Figs. S5 and S6). Therefore the calcination procedure (mentioned above) is highly favoured over the Soxhlet extraction procedure, since fully accessible and highly ordered pore systems are of tremendous importance in many applications including catalysis [89].

4. Conclusion

The *in-situ* combination of earth-abundant spinel MgFe₂O₄ NPs and mesoporous phenylene-bridged PMO with 3D cubic pore arrangement (KIT-6-type) was realized for the first time. The combination leads to a stabilization of the NPs in dispersion especially against acids without a loss of their optical or structural properties. Furthermore, the KIT-6-type MgFe₂O₄@phe-PMO exhibits highly ordered mesopores and high specific surface area (1164 m²g⁻¹). The insertion of the NPs into the phe-PMO network does not affect the pore ordering, which is very important and unique. Additionally, the presence of aromatic functional groups in the host material (phe-PMO) enables attractive interactions

with organic compounds. Surface functionalization can be easily added by post-synthetic strategies or even the choice of different bisilylated molecules for the formation of the PMO matrix. This opens up the way towards (photo)catalytic cascade reactions with such hybrid materials, where organic and inorganic components are involved.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.micromeso.2019.109783>.

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