

Applications of Mesoporous Silica Materials in Food – a Review

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Abstract

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Mesoporous silica materials have been developed for some applications in the health field. These solids are used for the controlled release of bioactive molecules, as catalysts in the synthesis of essential nutrients, as sensors to detect unhealthy products etc., with many applications in food technologies. By combining mesoporous silica materials with food, we can create healthier products, the products that improve our quality of life. The development of mesoporous materials applied to food could result in protecting bioactive molecules during their passage through the digestive system. For this reason, the controlled release of bioactive molecules is a very interesting topic for the discipline of food technology. The use of mesoporous silica supports as catalysts in the synthesis of nutrients and as sensors for the detection of unhealthy products, essential in food, is in great demand industrially for the manufacture of functional foods and films for food and industrial packaging. This review shows some examples of silica materials and their applications in food.

Keywords: bioactive molecules; healthier products; ordered solids

During the recent years, the number of studies of the controlled release of bioactive molecules, unhealthy product sensing, and bioactive molecules synthesis have been increasing. Nowadays, the combination of molecular and supramolecular concepts with material science to develop new hybrid systems is applied in the previous studies. There is an abundant potential for nanoparticle and microparticle materials use in future technologies including electronic and optoelectronic, mechanical, chemical, cosmetic, medical, drug, and food technologies (OKUYAMA 2006).

The controlled release of therapeutic drugs, vitamins, essential oils, nutraceutical and bioactive molecules in general, is a new and promising research field in life sciences. At the present time, silica mesoporous supports (SMPS) (KRESGE *et al.* 1992) are used as inorganic scaffoldings for the storage and release of drugs and organic molecules

(VALLET-REGÍ *et al.* 2001, 2007; MUÑOZ *et al.* 2003; CHEN *et al.* 2012). SMPS provide unique features such as stability, biocompatibility, and large load capacity. They have the possibility to include gate-like scaffoldings on the external surface for the design of nano-devices for on-command delivery applications (AZNAR *et al.* 2009). SMPS of different pore sizes and morphologies have been selected and used as inorganic scaffoldings in gated ensembles. SMPS can be prepared in different forms (from micrometric to nanometric) with tailor-made pores of around 2–10 nm. They show a very large specific surface area (up to 1200 m²/g) thus having a large load capacity, homogeneous porosity, high inertness, and are easy to functionalise.

On the other hand, the emergence and use of nanotechnologies in commercially available products, including nanotherapeutics, has necessitated the response of regulatory agencies to ensure

that these products are safely employed. While the bench scientists are at the forefront of the nanoparticle development and design, many are unaware of the regulatory requirements necessary to transform their laboratory discoveries into marketable products. Bench scientists (MARQUIS *et al.* 2011) performed a “thought experiment” using multifunctional mesoporous silica nanoparticles (MSN) synthesised in their laboratory, which they considered as a combination product. They made that experiment trying to understand the steps necessary for the pre-clinical approval from the Food and Drug Administration. This thought experiment illuminated the challenges associated with nanoparticle risk assessment and regulation.

As we know, synthetic amorphous silica has been used for many decades in a wide variety of industrial and consumer applications including food, cosmetics, and pharmaceutical products. Based on extensive physico-chemical, ecotoxicology, toxicology, safety, and epidemiology data, no environmental or health risks have been associated with these materials if produced and used under current hygiene standards and use recommendations (FRUIJTIER-POELLOTH 2012). Therefore none of the recent available data gives any evidence for a novel, hitherto unknown mechanism of toxicity that may raise concerns with regard to human health or environmental risks. On the other hand, the presence of nano-sized silica during *in vitro* digestion of foods containing silica as a food additive is an important feature described by PETERS *et al.* (2012). The results of their study showed that nano-sized (5–200 nm) silica was present in the saliva digestion stage in a relative amount of 5% to almost 40%. However, during the successive gastric digestion stage, this nano-sized silica disappeared. Importantly, when the low pH increased to neutral pH in the intestinal stage, nano-sized silica reappeared in even higher amounts than in the saliva stage. That study clearly showed that the human intestinal wall is most likely daily exposed to nano-sized silica particles.

In this review, we show the recent results in the design and preparation of capped materials and their use in on-command food applications.

Mesoporous materials as catalyst

Among the first works linking food and mesoporous materials were those presented described by DIAZ *et al.* (2000a,b, 2005) and MÁRQUEZ-ALVAREZ

et al. (2004), who used SMPS as catalysts in the synthesis of fatty acids, essential in food. The fatty acid monoesters of glycerol are valuable chemical products widely used as emulsifiers in the food, pharmaceutical, and cosmetics industries. There had already been two main preparative routes to obtain monoglycerides, but the investigations to optimise the yield of the monoderivative in both processes were of great interest. In the strategy for developing catalysts highly selective towards the monoderivative, MCM-41-type mesoporous silica functionalised with sulfonic acid groups were reported to catalyse selectively this reaction. These mesoporous catalysts combine a high acidity and a good accessibility to the active centres, owing to the presence of channels with large diameters exceeding 1.4 nm. THOMAS and RAJA (2006) reported that in using open-structure (nanoporous) solids, advantage may be taken of single-site catalytically active centres to affect an enormous range of conversions of organic compounds. In those active centres are regio-selectivity and shape-selectivity looming large. Typically, just one of the products (nylon-6), made by the “green”, environmentally benign bifunctional catalysts described by THOMAS and RAJA (2006), is in great demand industrially for the manufacture of apparel and other textiles; floor coverings; industrial yarns; engineering plastics, and films for food and industrial packaging.

On the other hand, the Claisen rearrangement of allyl phenyl ethers results in valuable products for fragrance, flavours, food, pharmaceuticals, and intermediate industries. It is typically initiated by using very high temperatures, normally above 200°C. Homogeneous acid catalysts are also used for this rearrangement, which YADAV and LANDE (2006) replaced profitably by using eco-friendly solid acids. One of the interests is nowadays focused also on biodiesel (MELERO 2009; SRINIVAS & SATYARTHI 2011). It is usually prepared from crude and refined triglyceride containing raw materials, such as vegetable oils, animal fats, and wastes-for instance waste cooking oil and yellow and brown grease. In this context, an appropriate solid acid catalyst would be of great interest for biodiesel production.

MOELANS *et al.* (2005) demonstrated new insights into the immobilisation of biomolecules in porous materials: the concept of thermally activated diffusion has successfully been applied to their immobilisation. This offered a possibility (*i*) to influence the immobilised amount and the cata-

lytic activity of some biomolecules in comparison with the classical method, and (ii) to re-think the overall concept of immobilisation of biomolecules in porous materials.

The use of nanoparticles to attach enzymes was reported in the late 1980s (WANG 2009; RICHARDS & CLOETE 2010). Since then, materials of various compositions, shapes, structures, and modified surfaces have been used to support biocatalysts. Nanoparticles made of silica, magnetite, and gold are the first group of nanomaterials applied for biocatalysis. Accordingly, enzymatic biocatalyst systems are being tackled dynamically at all size levels through efforts ranging from molecular level protein engineering and modification to nanoscale structure fabrication and microenvironment manipulation. They are used for the construction of microchip devices and macroscopic industrial bioreactors and devices. Other examples to attach enzymes have been reported recently. Rare sugars have many applications in the food industry, as well as in the pharmaceutical and nutrition industries. Xylitol dehydrogenase (XDH) can be used to synthesise various rare sugars enzymatically. However, the immobilisation of XDH has not been performed to improve the industrial production of rare sugars. Silica nanoparticles which have high immobilisation efficiency were selected by ZHANG *et al.* (2011a,b) from several carriers for the immobilisation of recombinant *Rhizobium etli* CFN42 xylitol dehydrogenase (ReXDH) and subjected to

characterisation. The immobilised ReXDH was employed to catalyse the biotransformation of xylitol to L-xylulose, a sugar that has been used in medicine and in the diagnosis of hepatitis. These results suggest that the immobilisation of ReXDH onto epoxy-silica nanoparticles has a potential industrial application in rare sugar production. For selective synthesis of lactobionic acid (LBA), GUTIERREZ *et al.* (2011) created a new method using silica materials as catalysts. Partial oxidation of lactose over an Au-based catalyst system using nanostructured silica materials with improved activity, selectivity, and stability was investigated as a novel chemo-catalytic approach. It is used for selective synthesis of LBA for therapeutic, pharmaceutical, and food grade applications. The main concepts of mesoporous materials as catalyst are given in Table 1.

Nutritional compounds synthesis

A further example linking food and silica materials was described by KISLER *et al.* (2003). As we know, mesoporous molecular sieves including MCM-41 appeared promising for the application as selective media for the separations of large molecules such as proteins, which are important in the food and pharmaceutical industries. However, many such applications involve aqueous solutions in which MCM-41 has a limited stability. The

Table 1. Mesoporous materials as catalyst

Mesoporous support	Catalyst	Molecule synthesised	Applications in food
MCM-41	sulfonic acids	fatty acids	emulsifier
MCM-41	Pd ₆ Ru ₆ /SiO ₂	nylon-6	food packaging
MCM-41	Ru ₆ Sn/SiO ₂	nylon-6	food packaging
HMS	heteropolyacid	6-allyl-2,4-di- <i>tert</i> -butylphenol	valuable products
Mesostructured solid	sulfonic acid	fatty acid methyl ester	biodiesel production
SBA-15	enzymes	biomolecules	food research
RL-SBA-15	enzymes	biomolecules	food research
MSU-X	enzymes	biomolecules	food research
Nanoporous silica glass	enzymes	sugars	food industry
Nanoscale carrier	enzymes	biofilms removal	food processing industry
Epoxy silica nanoparticles	xylitol dehydrogenase	L-xylulose	food industry
Silica nanostructured	Au	lactobionic acid	food industry

MCM-41 – mobil crystalline materials No 41; HMS – hexagonal mesoporous silica; SBA-15 – Santa Barbara amorphous type material; RL-SBA-15 – Rod-like SBA-15; MSU-X – Michigan State University

stability of silicate MCM-41 in aqueous solutions for up to 12 days was improved by silylation with hexamethyldisilazane (HMDS). Thus, hexamethyldisilazane was used to create a hydrophobic surface coating on both flat silica and MCM-41 in order to improve their stability in aqueous solutions.

Mesoporous materials as sensors in food

The last decades have witnessed a steady increase in the social and political awareness for the need of monitoring and controlling environmental and industrial processes. In the case of the nitrite ion, due to its potential toxicity for human health, the European Union has recently implemented a number of rules to restrict its levels in drinking water and food products. Although several analytical protocols have been proposed for nitrite quantification, none of them enables a reliable and quick analysis of complex samples. An alternative approach relies on the construction of biosensing devices using stable enzymes, with both high activity and specificity for nitrite. ALMEIDA *et al.* (2010) reviewed the current state-of-the-art in the field of electrochemical and optical biosensors. They used nitrite reducing enzymes as biorecognition elements and discussed the opportunities and challenges in this emerging market. Apart from that, recent trends in food safety promote an increasing search for trace compounds that can affect human health. Biogenic amines, the so-called natural amines with physiological significance, belong to this group of substances. Pyrylium-containing mesoporous materials were used for the chromo-fluorogenic sensing of biogenic amines in aqueous environment (GARCÍA-ACOSTA *et al.* 2006). This was one advanced goal in the development of selective probes for real samples that sense biogenic amines *via* a simple chromo-fluorogenic test but remain silent in the presence of fatty amines and amino acids. To achieve this goal, GARCÍA-ACOSTA *et al.* (2006) focused their attention on pyrylium compounds. As they and others had shown previously, such heterocyclic ring systems react with amines to give the corresponding pyridinium derivatives. In that example, a reactive pyrylium chromophore that was anchored into the inner hydrophobic pores of a mesoporous siliceous support was used. The solid demonstrates that the combination of molecular concepts and 3D solid state preorganised features

might open new attractive and synergistic hetero-supramolecular routes to enhanced recognition/sensing protocols for species of interest. Another example of the use of mesoporous materials as sensors was described for the determination of methylmercury in real samples using organically capped mesoporous inorganic materials capable of signal amplification (CLIMENT *et al.* 2009). Inspired by gated ion channels and pumps, the proposed sensing mechanism relies on the opening of a pore that is controlled by the interaction of a certain molecular stimulus (the target species, CH_3Hg^+) at the receptors that close the gate.

For the detection and removal of biogenic amines, SAAID *et al.* (2010) prepared three sorbent materials based on the crown ether ligands, 1-aza-18-crown-6,1,4,10,13-tetraoxa-7,16-diazacyclo octadecane and 4-aminobenzo-18-crown-6, respectively, by the chemical immobilisation of the ligand onto SMPS. The applicability of the sorbents for the extraction of biogenic amines by the batch sorption method was extensively studied. The optimised procedure was successfully applied for the separation of SPD (sensory processing disorder) in food samples prior to the reversed-phase high performance liquid chromatography separation.

Rapid determination of Sudan I (diazo-conjugate dye with the chemical formula of 1-phenylazo-2-naphthol) in foodstuffs is very important because it was found to be a carcinogen and its use in the food industry was banned (YANG & HE 2010). A rapid, sensitive, and convenient electrochemical method was developed for the determination of Sudan I based on the distinctive properties of mesoporous SiO_2 . The electrochemical responses of Sudan I were investigated. A sensitive oxidation peak was observed for Sudan I, and the peak current greatly increased at the mesoporous SiO_2 -modified electrode, which can be attributed to its large surface area and high accumulation efficiency. The effects of the pH, amount of mesoporous SiO_2 , scan rate, accumulation potential, and time were examined on the oxidation signals of Sudan I. The newly developed method was successfully used to detect and quantify Sudan I in hot chilli powder and juice samples.

Another example to increase the food quality was described by WEI *et al.* (2010). Norethisterone is one kind of widely used anabolic steroid hormones which can help to promote livestock growth and for some time had been illegally used for livestock breeding. The residues of norethisterone in animal

Table 2. Mesoporous materials as sensors in food

Mesoporous support	Sensor	Unhealthy molecule
HMS	enzyme	nitrite
MCM-41	pyrylium compounds	biogenic amines
MCM-41	mercaptopropyl groups	methylmercury
SMPS	crown ether ligands	biogenic amines
Mesoporous SiO ₂	mesoporous SiO ₂	Sudan I
Mesoporous SiO ₂	mesoporous SiO ₂	Sudan I
MSN	Ab ₂	norethisterone antigen
MSN	GMSNs	streptomycin residues
MCM-48	pyridine	nickel

HMS – hexagonal mesoporous silica; MCM-41 – mobil crystalline materials No 41; SMPS – silica mesoporous support; MSN – mesoporous silica nanoparticles; Ab₂ – secondary antibody; GMSNs – nanogold-assembled mesoporous silica; MCM-48 – mobil crystalline materials No 48; FIPHMs – fenpropathrin-imprinted porous hollow microspheres

food will harm people's health, therefore, it has been banned for the growth promotion purposes in livestock. In this study, amino-group functionalised MSN were prepared and used to immobilise Au nanoparticles, which was further utilised for the adsorption of horseradish peroxidase (HRP) and the secondary antibody Ab₂. The resulting nanoparticles, Au-MSN-HRP-Ab₂, were used as labels for immunosensors to detect norethisterone antigen. This new type of label for immunosensors may provide many potential applications for the detection of the growth hormone in animal derived food. Another immunosensor application in food technology was carried out by LIU *et al.* (2011). A facile and simple electrochemical immunoassay for ultrasensitive determination of streptomycin residues (STR) in food was designed. Nanogold-assembled mesoporous silica (GMSNs) as bionanotags on a three-dimensional redox-active organosilica-functionalised sensing interface was used. The methodology was validated with STR spiked samples including honey, milk, kidney, and muscle.

Nowadays, a new, sensitive, and low cost solid-phase extraction method using pyridine-functionalised MCM-48 mesoporous silica has been developed. It has been used for the extraction, pre-concentration, and electrothermal atomic absorption spectrometric determination of nickel and lead in food samples at ng/ml levels as described in (SADEGHI *et al.* 2011). The levels of nickel and lead in different types of vegetables grown in Shiraz and Rafsanjan (Iran), were de-

termined by electrothermal atomic absorption spectrometry. The use of two standard reference materials and also the comparison of the results with those of the standard reference procedure confirmed the accuracy of this method. Factors such as the flow rate of extraction and the type, pH, concentration, and volume of the eluent, were appraised. The effects of various ions on recovery were also investigated.

Another work using mesoporous materials as sensors was developed by ZHAO *et al.* (2012). In this paper, a novel chemiluminescence-molecular imprinting (CL-MI) sensor for the determination of fenpropathrin (used to control the range of insects, especially mites, in fruits and vegetables) in foodstuff was developed. Fenpropathrin-imprinted porous hollow microspheres (FIPHMs) were prepared using mesoporous silica particles as cores. The tests showed that the prepared sensor achieved high sensitivity and selectivity. The novel sensor has been successfully applied to the determination of fenpropathrin in food samples. The main concepts of mesoporous materials as sensors in food are given in Table 2.

Controlled release of bioactive molecules

The importance of α -tocopherol as an antioxidant in food applications is well-known, however, no complete antioxidant migration occurs from active packaging. HEIRLINGS *et al.* (2004) investigated the effects of polymer materials with dif-

ferent polarities, namely low density polyethylene (LDPE) and ethylene vinyl acetate (EVA), on the migration behaviour of α -tocopherol from active packaging. The antioxidant was also adsorbed onto silica materials, namely SBA-15 (Santa Barbara-15) and Syloblock, in order to protect the antioxidant during extrusion and to ensure a controlled and sufficient release during the shelf-life of the food product. The migration experiments were performed at $7.0 \pm 0.5^\circ\text{C}$ and 95% ethanol was used as a fatty food simulant. All films contained a high concentration of α -tocopherol, ~ 2000 mg/kg, to obtain an active packaging. The polymer matrix had a small influence on the migration profile. The migration of 80% of the total migrated amount of the antioxidant was retarded for 2.4 days by using LDPE instead of EVA. When α -tocopherol was adsorbed onto both silica materials, the migration of 80% of total migrated amount of the antioxidant was retarded for 3.4 days in comparison to pure α -tocopherol. No difference was seen between the migration profiles of the α -tocopherol adsorbed onto either silica material. In the case of pure α -tocopherol, 82% of the initial amount of α -tocopherol in the film migrated into the food simulant at a rather fast migration rate. In the case of adsorption on silica materials, total migration was observed. These anti-oxidative films can have positive food applications.

Curcumin is a yellow pigment found in the rhizomes of the plant *Curcuma longa*. Oligophenol is a major component of turmeric which is commonly used as a spice and food-colouring agent, and has been used in traditional Indian and Chinese medicine. *Trans*- β -carotene is another important bioactive organic compound or nutraceutical and is a model hydrophobic compound in studying drug delivery. These nutraceuticals appear promising in wound healing, which has been attributed to the presence of myofibroblasts, and to the compound enhancing fibronectin and collagen expression. However, the above mentioned properties of the nutraceuticals are yet to be realised in view of their full potential due to their poor bioavailability. For this reason, CLIFFORD *et al.* (2008) investigated the utility of mesoporous silica particles for encapsulating nutraceuticals and thereby serving as a molecular tracker, a drug carrier, and a controlled drug release system. Mesoporous silica particles were suggested as useful carriers because of their stability, controllable pore diameter, and excellent biocompatibility. The authors studied the

ability to insert nutraceuticals into the structure of mesoporous silica particles during the formation of rigid mesospheres involving the micelle template. The rate of release of the curcumin and *trans*- β -carotene in the silica particles was also reported under physiological pH, to determine the potential application of these silica particles as a method of delivering biologically active molecules to the body.

A study on the controlled release of vitamin B₂ (an important micronutrient in diet) in pure water from mesoporous silica materials was reported by BERNARDOS *et al.* (2008). Mesoporous silica-based materials contain pH- and anion-controlled nano-supramolecular gate-like ensembles built up by anchoring suitable polyamines on the external surface. This solid contains the vitamin (the delivered molecule) onto the pores, whereas the amine-based gate-like ensemble is anchored on the pore outlets. The delivery studies in water were carried out at pH 2 and 7. At pH 2, all the anions studied (sulphate, phosphate, GMP, and ATP) strongly hindered the vitamin release, whereas at pH 7 the delivery was observed for sulphate and GMP, the gate remaining closed in the presence of ATP and phosphate. The remarkable anion-controllable response of the gate-like ensemble at a certain pH can be explained in terms of anion complex formation with the tethered polyamines. The pH-controlled gate-like scaffoldings might be a suitable prototype for the development of orally applicable delivery systems designed to have a particular ability to protect the cargo from the acidic conditions in the stomach (acid pH, gate closed) but will release the load in the intestine (basic pH, gate open). For vitamin B₃ controlled release, ordered mesoporous silica hollow microspheres with distinguished characteristics of interconnected porosity of their thin outer walls were developed by KAPOOR *et al.* (2010). Food grade emulsifiers polyglycerol esters of fatty acids (PGEFA) were used as a soft-template and *n*-decane as a swelling agent. The interconnected pore channels that extend from the outside of the microsphere shell to its inside were used to fill the mesoporous silica microspheres for enhanced encapsulation and cumulative *in vitro* release of vitamin B₃. A considerable rate of pharmacokinetics using a simple pH trigger mechanism for the delivery systems was observed.

BERNARDOS *et al.* (2009) also described the synthesis of a lactose-capped SMPS that is selectively

Table 3. Controlled release of bioactive molecules

Mesoporous support	Bioactive molecule loaded	Release mechanism	Properties in food
SBA-15	α -tocopherol	migration	antioxidant
SMPS	curcumin	migration	nutraceuticals
SMPS	oligophenol	migration	nutraceuticals
SMPS	trans- β -carotene	migration	nutraceuticals
MCM-41	vitamin B ₂	pH changes	micronutrient
Mesoporous silica Hollow	vitamin B ₃	pH changes	micronutrient
MCM-41	dye	β -D-galactosidase presence	nutrients
MCM-41	AITC	adsorption-desorption	natural antimicrobial
SBA-15	AITC	adsorption-desorption	natural antimicrobial
SMPS	(-)-menthol	adsorption-desorption	anesthetic/counterirritant

SBA-15 – Santa Barbara amorphous type material; SMPS – silica mesoporous support; MCM-41 – mobil crystalline materials No 41; AITC – allyl isothiocyanate

uncapped by the rupture of a glycosidic bond using β -D-galactosidase. The enzyme β -D-galactosidase is a glycoside hydrolase involved in the hydrolysis of the disaccharide lactose into the monosaccharides galactose and glucose. In humans, β -D-galactosidase is present predominantly along the brush border membrane of the differentiated enterocytes lining the vili of the small intestine, for this reason this system is a suitable material in food applications.

At the present time, mesoporous silica structures have been synthesised as MCM-41 and SBA-15 at two different mole ratios of their constituents to test their capacity and feasibility for the controlled release of the natural antimicrobial allyl isothiocyanate (AITC) (PARK *et al.* 2011, 2012; PARK & PENDLETON 2012). Pore filling by vapour phase AITC approached 100%. The controlled release as desorption was dictated by the pore size distribution of each material with up to 90% of the available AITC desorbed over 96 hours. The release from the SBA-15 systems occurred as a “burst release” with 65% desorbed in the first 12 h compared with only 20% from the MCM-41 systems. The antimicrobial activity of the released (vapour phase) AITC was compared with that of liquid AITC in tests with the microorganisms *Escherichia coli*, *Bacillus cereus*, and *Pichia anomola*. The lethal activity of the released AITC against these microorganisms was unaffected by adsorption and desorption processes, demonstrating that the MCM-41 and SBA-15 mesoporous silica structures represent a novel controlled release vector against the selected food-borne pathogenic microorganisms. Another example of vapour-phase

controlled release was described here. A series of nanoporous silica materials were prepared as adsorbents for volatile (-)-menthol, a molecule widely used in food, pharmacy, and cosmetics. A vesicular silica material with a thick wall and hydrophobic functional groups was shown to possess the slowest release performance (ZHANG *et al.* 2011a,b). The main concepts of the controlled release of bioactive molecules are given in Table 3.

CONCLUSIONS

This review reports recent research into the design of gated mesoporous siliceous materials for cargo controlled release using different stimuli, and their applications in food. These capped materials can find applications in the design of novel and creative ways to deliver drugs, nutrients, and bioactive molecules. In fact, mesoporous supports display characteristics that usually cannot be found in classical drug delivery systems (such as polymers, dendrimers, micelles, etc) due to their unique properties. In summary, these findings, and some other recently reported, are opening new perspectives in relation to the use of mesoporous hybrid solids with gating functionalities in the field of food.

References

- ALMEIDA M.G., SERRA A., SILVEIRA C.M., MOURA J.J.G. (2010): Nitrite biosensing via selective enzymes – A long but promising route. *Sensors*, **10**: 11530–11555.

- AZNAR E., MARTINEZ–MANEZ R., SANCENON F. (2009): Controlled release using mesoporous materials containing gate-like scaffoldings. *Expert Opinion on Drug Delivery*, **6**: 643–655.
- BERNARDOS A., AZNAR E., COLL C., MARTÍNEZ–MAÑEZ R., BARAT J.M., MARCOS M.D., SANCENÓN F., BENITO A., SOTO J. (2008): Controlled release of vitamin B₂ using mesoporous materials functionalized with amine-bearing gate-like scaffoldings. *Journal of Controlled Release*, **131**: 181–189.
- BERNARDOS A., AZNAR E., MARCOS M.D., MARTÍNEZ–MÁÑEZ R., SANCENÓN F., SOTO J., BARAT J.M., AMORÓS P. (2009): Enzyme-responsive controlled release using mesoporous silica supports capped with lactose. *Angewandte Chemie International Edition*, **48**: 5884–5887.
- CHEN Q., LARISMAA J., KESKI-HONKOLA A., VILONEN K., SODERBERG O., HANNULA S.P. (2012): Effect of synthesis time on morphology of hollow porous silica microspheres. *Materials Science-Medziagotyra*, **18**: 66–71.
- CLIFFORD N.W., IYER K.S., RASTON C.L. (2008): Encapsulation and controlled release of nutraceuticals using mesoporous silica capsules. *Journal of Materials Chemistry*, **18**: 162–165.
- CLIMENT E., MARCOS M.D., MARTÍNEZ–MÁÑEZ R., SANCENÓN F., SOTO J., RURACK K., AMORÓS P. (2009): The determination of methylmercury in real samples using organically capped mesoporous inorganic materials capable of signal amplification. *Angewandte Chemie International Edition*, **48**: 8519–8522.
- DÍAZ I., MÁRQUEZ-ALVAREZ C., MOHINO F., PÉREZ-PARIENTE J., SASTRE E. (2000a): Combined alkyl and sulfonic acid functionalization of MCM-41-type silica – Part 1. Synthesis and characterization. *Journal of Catalysis*, **193**: 283–294.
- DÍAZ I., MÁRQUEZ-ALVAREZ C., MOHINO F., PÉREZ-PARIENTE J., SASTRE E. (2000b): Combined alkyl and sulfonic acid functionalization of MCM-41-type silica – Part 2. Esterification of glycerol with fatty acids. *Journal of Catalysis*, **193**: 295–302.
- DÍAZ I., MOHINO F., BLASCO T., SASTRE E., PÉREZ-PARIENTE J. (2005): Influence of the alkyl chain length of HSO₃-R-MCM-41 on the esterification of glycerol with fatty acids. *Microporous and Mesoporous Materials*, **80**: 33–42.
- FRUIJTIER-POELLOTH C. (2012): The toxicological mode of action and the safety of synthetic amorphous silica – A nanostructured material. *Toxicology*, **294**: 61–79.
- GÁRCIA-ACOSTA B., COMES M., BRICKS J.L., KUDINOVA M.A., KURDYUKOV V.V., TOLMACHEV A.I., DESCALZO A.B., MARCOS M.D., MARTÍNEZ–MÁÑEZ R., MORENO A., SANCENÓN F., SOTO J., VILLAESCUSA L.A., RURACK K., BARAT J.M., ESCRICHE I., AMORÓS P. (2006): Sensory hybrid host materials for the selective chromo-fluorogenic detection of biogenic amines. *Chemical Communications*, 2239–2241.
- GUTIERREZ L.F., HAMOUDI S., BELKACEMI K. (2011): Selective production of lactobionic acid by aerobic oxidation of lactose over gold crystallites supported on mesoporous silica. *Applied Catalysis A: General*, **402**: 94–103.
- HEIRLINGS L., SIRÓ I., DEVLIEGHIERE F., BAVEL VAN E., COOL P., DE MEULENAER B., VANSANT E.F., DEBEVERE J. (2004): Influence of polymer matrix and adsorption onto silica materials on the migration of α -tocopherol into 95% ethanol from active packaging. *Food Additives and Contaminants*, **21**: 1125–1136.
- KAPOOR M.P., VINU A., FUJII W., KIMURA T., YANG Q.H., KASAMA Y., YANAGI M., JUNEJA L.R. (2010): Self-assembly of mesoporous silicas hollow microspheres via food grade emulsifiers for delivery systems. *Microporous and Mesoporous Materials*, **128**: 187–193.
- KISLER J.M., GEE M.L., STEVENS G.W., O’CONNOR A.J. (2003): Comparative study of silylation methods to improve the stability of silicate MCM-41 in aqueous solutions. *Chemistry of Materials*, **15**: 619–624.
- KRESGE C.T., LEONOWICZ M.E., ROTH W.J., VARTULI J.C., BECK J.S. (1992): Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature*, **359**: 710–712.
- LIU B., ZHANG B., CUI Y., CHEN H., GAO Z., TANG D. (2011): Multifunctional gold-silica nanostructures for ultrasensitive electrochemical immunoassay of streptomycin residues. *ACS Applied Materials and Interfaces*, **3**: 4668–4676.
- MÁRQUEZ-ALVAREZ C., SASTRE E., PÉREZ-PARIENTE J. (2004): Solid catalysts for the synthesis of fatty esters of glycerol, polyglycerols and sorbitol from renewable resources. *Topics in Catalysis*, **27**: 105–117.
- MARQUIS B.J., MAURER-JONES M.A., ERSIN O.H., LIN Y.S., HAYNES C.L. (2011): The bench scientist’s perspective on the unique considerations in nanoparticle regulation. *Journal of Nanoparticle Research*, **13**: 1389–1400.
- MELERO J.A., IGLESIAS J., MORALES G. (2009): Heterogeneous acid catalysts for biodiesel production: current status and future challenges. *Green Chemistry*, **11**: 1285–1308.
- MOELANS D., COOL P., BAEYENS J., VANSANT E.F. (2005): Immobilisation behaviour of biomolecules in mesoporous silica materials. *Catalysis Communications*, **6**: 591–595.
- MUÑOZ B., RAMILA A., PEREZ-PARIENTE J., DIAZ I., VALLET-REGI M. (2003): MCM-41 organic modification as drug delivery rate regulator. *Chemistry of Materials*, **15**: 500–503.
- OKUYAMA K., ABDULLAH M., LENGGORO I.W., ISKANDAR F. (2006): Preparation of functional nanostructured particles by spray drying. *Advanced Powder Technology*, **17**: 587–611.

- PARK S.-Y., BARTON M., PENDLETON P. (2011): Mesoporous silica as a natural antimicrobial carrier. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **385**: 256–261.
- PARK S.-Y., PENDLETON P. (2012): Mesoporous silica SBA-15 for natural antimicrobial delivery. *Powder Technology*, **223**: 77–82.
- PARK S.-Y., BARTON M., PENDLETON P. (2012): Controlled release of allyl isothiocyanate for bacteria growth management. *Food Control*, **23**: 478–484.
- PETERS R., KRAMER E., OOMEN A.G., HERRERA RIVERA Z.E., OEGEMA G., TROMP P.C., FOKKINK R., RIETVELD A., MARVIN H.J.P., WEIGEL S., PEIJNENBURG A.A.C.M., BOUWMEESTER H. (2012): Presence of nano-sized silica during *in vitro* digestion of foods containing silica as a food additive. *ACS Nano*, **6**: 2441–2451.
- RICHARDS M., CLOETE T.E. (2010): Nanozymes for biofilm removal. In: CLOETE E.T., DE KWAADSTENIET M., BOTES M., LÓPEZ-ROMERO J.M. (eds): *Nanotechnology in Water Treatment Applications*. Caister Academic Press, Norwich: 89–101.
- SAAD M., SAAD B., AB RAHMAN I., ALI A.S.M., SALEH M.I. (2010): Extraction of biogenic amines using sorbent materials containing immobilized crown ethers. *Talanta*, **80**: 1183–1190.
- SADEGHI O., TAVASSOLI N., AMINI M.M., EBRAHIMZADEH H., DAEI N. (2011): Pyridine-functionalized mesoporous silica as an adsorbent material for the determination of nickel and lead in vegetables grown in close proximity by electrothermal atomic adsorption spectroscopy. *Food Chemistry*, **127**: 364–368.
- SRINIVAS D., SATYARTHI J.K. (2011): Biodiesel production from vegetable oils and animal fat over solid acid double-metal cyanide catalysts. *Catalysis Surveys from Asia*, **15**: 145–160.
- THOMAS J.M., RAJA R. (2006): The advantages and future potential of single-site heterogeneous catalysts. *Topics in Catalysis*, **40**: 3–17.
- VALLET-REGI M., RÁMILA A., DEL REAL R.P., PÉREZ-PARIENTE J. (2001): A new property of MCM-41: drug delivery system. *Chemistry of Materials*, **13**: 308–311.
- VALLET-REGI M., BALAS F., ARCOS D. (2007): Mesoporous materials for drug delivery. *Angewandte Chemie International Edition*, **46**: 7548–7558.
- WANG P. (2009): Multi-scale features in recent development of enzymic biocatalyst systems. *Applied Biochemistry and Biotechnology*, **152**: 343–352.
- WEI Q., XIN X.D., DU B., WU D., HAN Y.Y., ZHAO Y.F., CAI Y.Y., LI R., YANG M.H., LI H. (2010): Electrochemical immunosensor for norethisterone based on signal amplification strategy of graphene sheets and multienzyme functionalized mesoporous silica nanoparticles. *Biosensors and Bioelectronics*, **26**: 723–729.
- YADAV G.D., LANDE S.V. (2006): Selective Claisen rearrangement of allyl-2,4-di-*tert*-butylphenyl ether to 6-allyl-2,4-di-*tert*-butylphenol catalysed by heteropolyacid supported on hexagonal mesoporous silica. *Journal of Molecular Catalysis A: Chemical*, **243**: 31–39.
- YANG X., HE D. (2010): Rapid determination of banned Sudan I in foodstuffs using a mesoporous SiO₂ modified electrode. *Journal of AOAC International*, **93**: 1537–1541.
- ZHANG Y.W., TIWARI M.K., JEYA M., LEE J.K. (2011a): Covalent immobilization of recombinant *Rhizobium etli* CFN42 xylitol dehydrogenase onto modified silica nanoparticles. *Applied Microbiology and Biotechnology*, **90**: 499–507.
- ZHANG J., YU M.H., YUAN P., LU G.Q., YU C.Z. (2011b): Controlled release of volatile (–)-menthol in nanoporous silica materials. *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, **71**: 593–602.
- ZHAO P., YUA J., LIUB S., YANA M., ZANGA D., GAO L. (2012): One novel chemiluminescence sensor for determination of fenpropathrin based on molecularly imprinted porous hollow microspheres. *Sensors and Actuators B: Chemical*, **162**: 166–172.

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