Breakthroughs in Mesoporous Composite Materials

Mesoporous materials have attracted a great deal of attention due to their extremely high surface area, uniform and tunable pore structure (2–50nm in diameter), and have been investigated extensively since its invention. Unfortunately, their catalytic properties are far away from the expectation due to their amorphous and inert framework and poor stability. This research project is aimed at the design and synthesis of mesoporous-based composites, their catalytic properties and application exploration. As the main contributors to the achievements, Profs. SHI Jianlin, CHEN Hangrong, GAO Qiuming, ZHANG Wenhua and YAN Dongsheng, all from the CAS Shanghai Institute of Ceramics, have made a series of discoveries of great significance to the design and development of composite materials at nano scale and their application in catalysis.

Prof. SHI Jianlin is now a professor and Ph.D supervisor in the CAS Shanghai institute of Ceramics and director of the State key Lab of High performance Ceramics and Superfine Microstructure. Currently his research involves inorganic nanomaterials, mesoporous-based nanocomposites and their catalytic properties, biomedical and optical applications, and transparent ceramics.
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Primary discoveries —

The design strategy of the host-guest and core/shell composite materials is established. The design strategies of two kinds of mesoporous composites were proposed. The first one, based on the loading of guest materials into the pore channels of mesoporous materials which acted as the host, various types of guest materials were loaded into the pore channels with controlled existing forms. The other one is the design of a core/shell structure by using functional particles as core and mesoporous silica as the shell, combining functionalized feature and mesoporous structure into one. Prof.SHI and his colleagues are the first to propose and synthesize these two kinds of mesoporus-based composites.

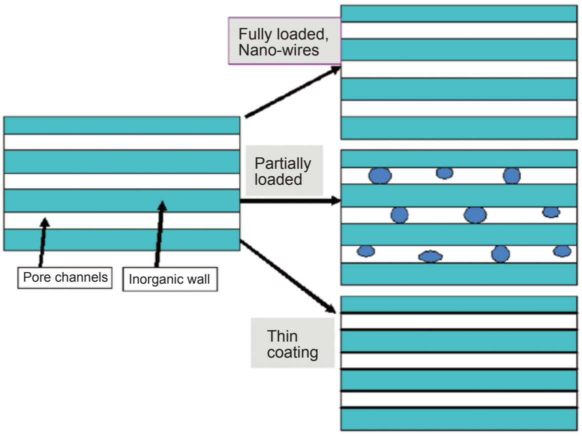


Figure 1. Shown is the design strategy of the host-guest mesoporous composites with guests loaded in the pore channels of a mesoporous host.

In the synthesis of host-guest composites, the pore channels are used as "micro-reactor" for the loading of the guest precusors (reactants) and the *in-situ* reactions were initiated within the channels, and the guest materials can be *in-situ* synthesized with controlled existing forms of continuous nanowires (full loading), highly dispersed nanoparticles (partial loading) and untra-thin coating on the pore inner surface (thin coating). A layer-by-layer coating strategy was developed to synthesize core-shell structured mesoporous composites, as shown in Figure 2.

Silane coupling agent complexing/grafting approaches for inorganic compound or organic molecule-loaded

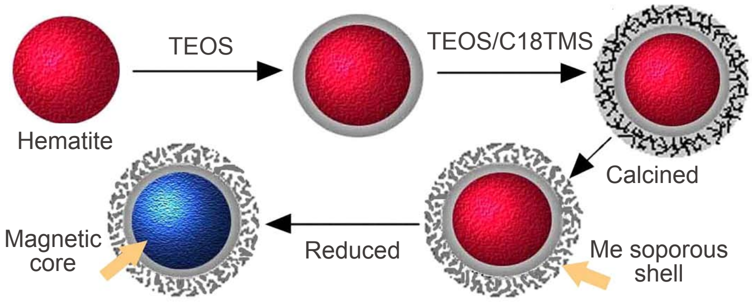
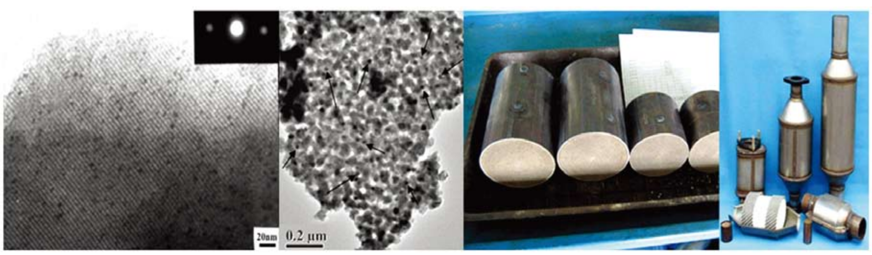


Figure 2. This is the synthesis strategy for the magnetic core-mesoporous shellstructured composite.

host-guest composites for heterogeneous catalysis are developed. With the help of aboundant Si-OH groups, the pore surface was firstly modified with silane molecules and thus the metal ions can be complexed by the functional groups on silane molecules. After oxidation, sulfidation and phosphidation, the metal oxides, sulfides and phosphides can be loaded into the pore channels. Alternatively, organic molecuels can be firstly chemically linked to silanes and then be introduced into the pore channels by the reaction between the silane and the Si-OH groups on the pore wall. This is a general strategy and various kinds of inorganic and/or organic compounds can be loaded into the host. Some of synthesized host-guest materials showed excellent recyclable catalytic properties such as olefin metathesis reactions catalyzed by Ru-Carbene loaded host-guest materials.

Selective modification-*in-situ* reduction approaches for the noble metal loaded host-guest composites are developed and its catalytic performance for Heck reactions is studied. Though the silane coupling agent complexing approach can be applied to various compounds, it was not applicable to the loading of noble metals into the mesopore channels. A new selective modification-*in-situ* reduction approach was developed, in which the outer surface was poisoned by inert $Si\text{-}CH_3$ groups, then the Si-OH groups were converted into Si-H groups after the extraction of surfactants, and then the introduced noble metal ions will be *in-situ* reduced into metals by the Si-H groups at room temperature. In addition, dendrimers were used to modify the pore channels and then noble metal nanoparticle can be loaded into the pore channels. Thin layers of noble metal nanoparticles were then coated onto the pore inner surface, which showed excellent heterogeneous catalytic activity for Heck reactions with extremely low amount of noble metal catalysts.

The researchers have established the reactant co-introduction-*in-situ* reaction approach for noble metal-loaded, non-silica-based composites of crystallized framework and realized its application in three-way catalysis for automobil exhaust treatments. The above surface modification methods cannot be applied to non-silica hosts due to the absence of M-OH groups (M=metals) on the pore surface. Then a novel reactant-co-introduction approach was developed to load noble metals into the pore channels of non-silica, for instance, ZrO_2 mesoporous host. The noble metal-loaded mesoporous zirconia was further extended and modified to be Pt/Pd/Rh-loaded mesoporous La-Zr(Ce)O_2 composites, which showed excellent three-way catalysis properties (Euro-IV/V standard) with about half noble metal consumption. Small-sized sample converter (honey combs coated with these catalysts) were tested by the national automobile testing center in Tianjin City, which showed an ignition temperature lower than 250^{o}C. Conversion rates for CO, NOx and CxHy were all higher than 95%. A series of road tests then were completed for five types of cars with Euro-IV discharge standard. The production and scale sales of full-sized honeycomb converters were realized in the second half of 2010.



TEM images of ordered Pt-loaded mesoporous ZrO_2 (left), Pt/Pd/Rh-loaded mesoporous Zr(Ce)O_2 composite with crystallized framework after ageing at 1000oC (middle), and the full-sized honeycomb converters with the three-way catalysts coated (right).