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Catalyst nanoconfinement and promotion for synthesis of platform molecules from renewable feedstocks

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1. Introduction

The bio-sourced platform molecules manufactured from biomass, used plastics and organic waste are supplying alternative and sustainable solutions for reduction of emissions of greenhouse gases and for growing energy demand. Fischer-Tropsch synthesis is a technology that converts renewable feedstocks via biosyngas (H_2 -CO) to liquid fuels and chemicals. The Fischer-Tropsch technology suffers from insufficient selectivity to the target products and catalytic stability problems.

Thus, new strategies for the selective production of fuels and chemicals from syngas generated from renewable and alternative feedstocks are highly desirable. Several efforts have been made to improve the catalytic performance of Fischer-Tropsch catalysts, either by regulating the active species, supports, adding promoters, or by optimizing the reaction conditions. Both nanoconfinement of active phase into porous matrices and conducting catalytic reaction in nanoconfined spaces may potentially bring numerous important benefits for the production of the target products from syngas.

In this lecture, we consider three examples of nanoconfinement for improvements of the production rate and selectivity to specific products in CO hydrogenation: **nanoconfinement in nanoreactors**, **nanoconfinement in zeolites** and **nanoconfinement in carbon nanotubes**. General conclusions about the nanoconfinement effects for the synthesis for fuels and chemicals are then drawn on the basis of the conducted research.

3. Results and discussion

Nanoreactors represent a new generation of heterogeneous catalysts with excellent catalytic stability due to their specific structure, which consists of a core, commonly the active phase, surrounded by a porous shell. We report a new strategy for the control of hydrocarbon selectivity in Fischer-Tropsch synthesis by nanoconfinement of ruthenium nanoparticles in silica yolk-shell nanoreactors prepared in water/oil (W/O) microemulsion. The sizes of nanoreactors have been varied by changing the microemulsion composition. Nanoreactors prepared with smallest internal volume exhibited a restriction of hydrocarbon chain length growth during Fischer-Tropsch synthesis. The chain length of the produced hydrocarbons was strongly affected by the nanoreactor volume.

Zeolites appear to be among the best candidates for introducing an acidic function because of their high thermal stability, acidity and unique nanometric porous network. There are a number of catalytic reactions (hydrocracking, aromatisation, dimethyl ether synthesis etc.) where metal-zeolite composites have been efficiently used. Bifunctional catalysts combining a Fischer-Tropsch active phase and a zeolite provide an opportunity for manufacturing specific hydrocarbons in a single step. The nanoconfinement of active phase in the zeolite matrix is extremely important for obtaining higher selectivity. We elaborated two strategies for the design of the zeolite composites with nanoconfined nanoparticles. The first strategy is based on the selective extraction of metal species from the zeolite outer surface using bulky acid molecules. The second strategy involves sacrificial carbon templates for encapsulation of metal nanoparticles inside the zeolite crystals. Both strategies allow selective synthesis of isomerized hydrocarbons from syngas.

Carbon nanotubes were used to evaluate and to optimize the effects of the nanoconfinement and promotion on the catalytic performance of iron catalysts supported by carbon nanotubes for synthesis of light olefins. The size of iron nanoparticles inside the carbon nanotubes was limited by the pore diameter. Their sintering was significantly reduced. Iron reduction and carbidization proceeded much easily for iron species confined inside carbon nanotubes and promoted with Bi and Pb. Iron nanoconfinement inside carbon nanotubes combined with the promotion with Bi or Pb result in a 10-fold higher yield of light olefins.

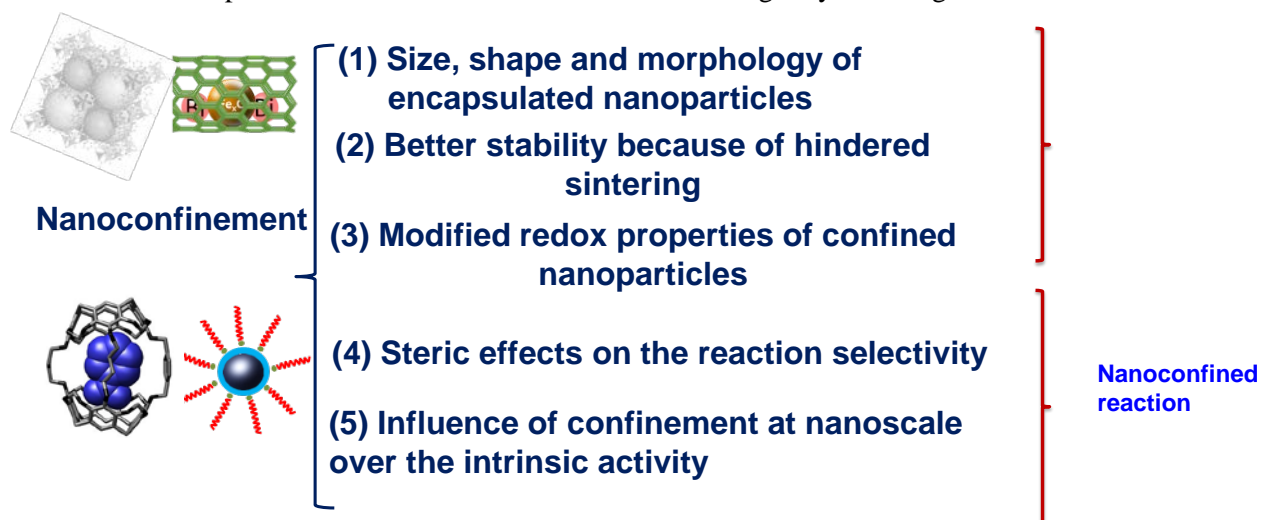


Figure 1. Multiple effects of nanoconfinement on the catalyst structure and catalytic reaction

3. Conclusion

Nanoconfinement of active phase inside porous materials results in several major effects on the nanoconfined active phase and on the nanoconfined reaction. First, the size of encapsulated nanoparticles can be controlled by the pore diameter in nanoconfined materials. The nanoparticles inside the pores and cavities can adapt their shape and morphology. Second, the nanoconfinement can prevent the nanoparticles from sintering during the catalyst activation and catalysis. Consequently, catalyst deactivation can be slowed down, resulting in the enhanced and stable catalytic performance. Third, nanoconfinement can modify the reducibility of confined species. Fourth, the nanoconfinement of the active phase can restrain the movement of reagents, intermediates and products via modification entropy and enthalpy of adsorbed reaction intermediates and transition states. Finally, the electronic properties of nanoparticles can be affected by nanoconfinement. Nanoconfinement emerges as efficient strategy for the design of new selective catalytic materials and processes.