# Metal nanoparticles in cubic mesostructures for regenerable deep desulfurization of warm syngas

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## Introduction

Gasification of coal or biomass to syngas followed by catalytic synthesis of liquid hydrocarbons or oxygenates provides a feasible strategy to meet the increasing demand for transportation fuels. A significant challenge is posed by sulfur present in the syngas, which poisons the catalysts even at low part per million by volume (ppmv) levels. Although technical approaches exist for removal of sulfur species to the required less than 60 part per billion by volume (ppbv) level, they are rather costly and energy intensive, employing solvents at ambient or lower temperature and backup sacrificial adsorbents. Since catalytic processes for the production of fuels and chemicals typically operate in the range of 200-300$^oC$, a process capable of removing sulfur at such an intermediate temperature range is preferred. Several warm cleanup technologies have been developed based on metal oxide sorbents, primarily zinc oxide-containing materials. However sulfur can only be removed over regenerated zinc oxide absorbents to a few ppmv, insufficient for chemical synthesis work.

The removal strategy used in this work is based on the excellent gettering ability of metals (Ni, Cu, Fe) toward sulfur gases, the same reason for their readily being poisoned when used as synthesis catalysts. Surface chemisorption rather than bulk sulfide formation removes sulfur from warm syngas to the required ppbv levels. The use of metal-based sulfur getters has been exploited thus far only for sacrificial adsorbents [1]. Development of regenerable metal adsorbents has been stymied by the strong tendency of the metals to sinter or aggregate during the regeneration process, losing surface area and therefore sulfur adsorption capacity. This work reports the synthesis and application of a class of unique metal-based adsorbents in which small metal particles are contained and stabilized within cubic mesoporous silica structures. The isolation and stabilization of the small metal particles allows regeneration of the sulfur-loaded adsorbents with minimal sintering and loss of capacity.

## Materials and Methods

The three-dimensional cubic pore structure mesoporous silica SBA-16 was prepared according to published procedures [2,3]. Nickel-copper alloy was loaded into SBA-16 supports by incipient wetness using metal nitrates aqueous solution. Desulfurization was carried out in a fixed bed reactor at 300$^oC$ using simulated wet biomass or coal syngases. Typical regeneration was carried out in a reverse flow mode by the following steps: (1) ramping from 300$^oC$ to 700$^oC$ in air; (2) holding at 700$^oC$ in Ar for 4 hours; (3) reducing in 5% clean dry syngas at 500$^oC$ for 4 hours.

## Results and Discussion

By trapping metal nanoparticles in cubic mesostructured silica (SBA-16), a new class of regenerable adsorbents that efficiently remove sulfur-containing impurities from warm syngases was developed. Operating via a surface chemisorption mechanism, the metal nanoparticles reduce the sulfur concentration in warm wet syngases to less than 60 ppbv at 300$^oC$. A sequential oxidation-reduction treatment can effectively regenerate the sulfur-loaded adsorbent, resulting in minimal loss of capacity in subsequent sulfur-removal cycles. The three-dimensional interconnected cage structure of the mesoporous support allows good accessibility of sulfur gases to the active sites and confines the metal particles within its nano-sized cages. This confinement hinders metal particle migration and sintering under the harsh conditions of desulfurization and regeneration, which typically occur with the conventional sacrificial metal adsorbents. An integrated system with a ZnO-based absorbent upstream and the Ni-Cu/SBA-16 adsorbent downstream gives both high sulfur capacity and low sulfur slip in a fully regenerable sulfur sorption system. Figure 1 gives the regenerable sulfur removal performance of a 28.8 wt% Ni-Cu/SBA-16 adsorbent.

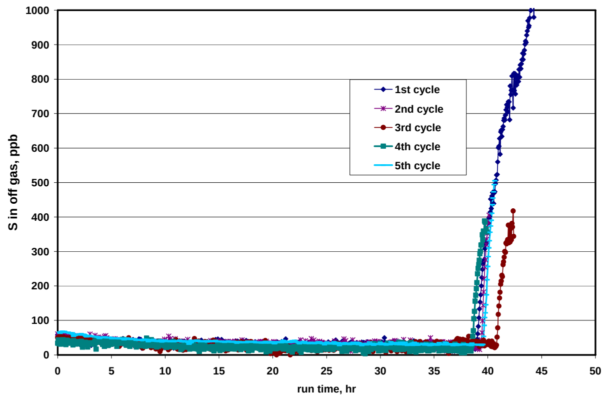


**Figure 1.** Regenerable sulfur removal performance of 28.8 wt% Ni-Cu/SBA-16 adsorbent

## Significance

This solid adsorbent-based warm deep desulfurization approach can provide economic advantages compared with existing solvent-based technologies, and may find general use for warm cleanup of gasifier-derived syngas for synthesis applications and of hydrocarbon fuel reformates for fuel cell applications. This work also provides new insights into the stability of nanoparticles within controlled mesostructures. Metal and metal oxide nanoparticles supported on high surface area materials are widely used in industry, but preventing nano-sized particle sintering has remained a great challenge. Our study suggests that the stability and activity of nanoparticles may be substantially enhanced by judicious choice of the pore architecture that confines them.

## References

1. Rostrup-Nielsen, J. R., Sehested, J. & Norskov, J. K. *Advances in Catalysis* 46, 65 (2002).
2. Sakamoto, Y. et al., *Nature* 408, 449 (2000).
3. Zhao, D. Y., Huo, Q. S., Feng, J. L., Chmelka, B. F. & Stucky, G. D. *J. Am. Chem. Soc.* 120, 6024 (1998).