High Pressure Synthesis of Periodic Mesoporous Silica with Crystalline Pore Walls

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An Energy Frontier Research Center

The *Next Generation Mesoporous Materials* Project

EFree Mission:

To accelerate the discovery and synthesis of new energy materials using extreme conditions.

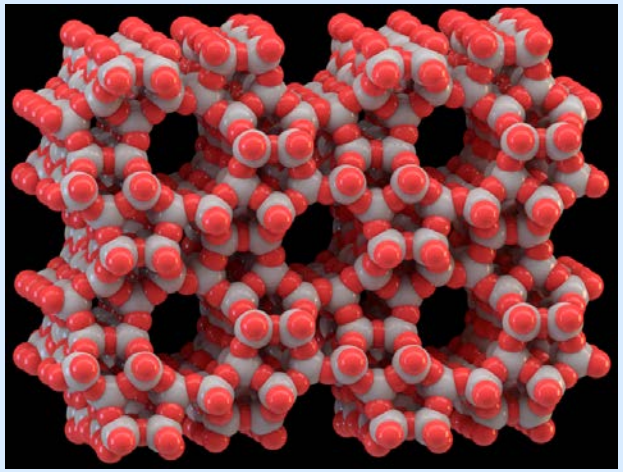
Goal of the Mesoporous Materials Project*:*

To obtain mesoporous and mesostructured crystalline materials through templated synthetic routes at high pressure for catalysis and related applications.

Current Research Objectives:

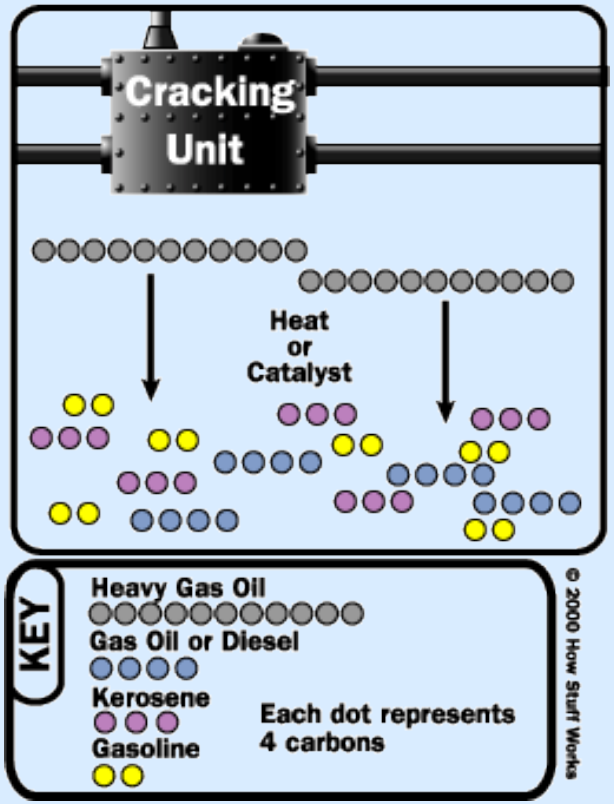
To synthesize mesoporous aluminosilica material with crystalline channel walls at high pressure, and to grow mesoporous quartz single crystal under hydrothermal conditions, so that these materials may act as catalyst or catalyst support which would be hydrothermally stable in high temperature catalysis .

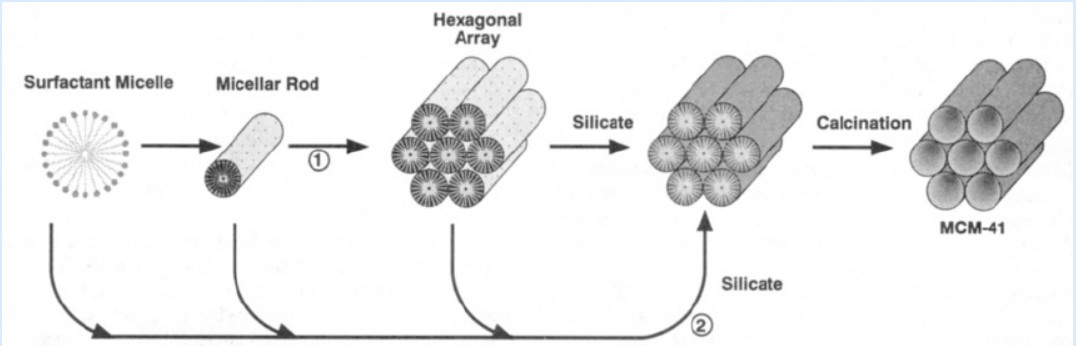
Background



ZSM-5

Zeolite:
The small pore size restrains the difusion of large molecules in the narrow micropores.





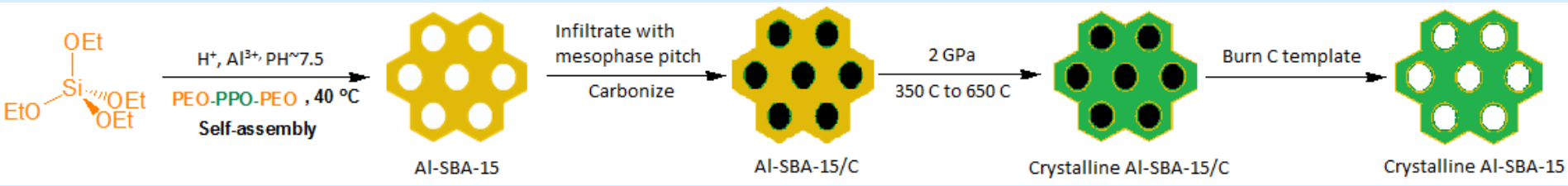
Beck et al. *JACS,* **1992,** 114, 10834.

Mesoporous silica:
Lack of crystallinity
Low hydrothermal stability
Lack of acidity

Nanocasting at High Pressure

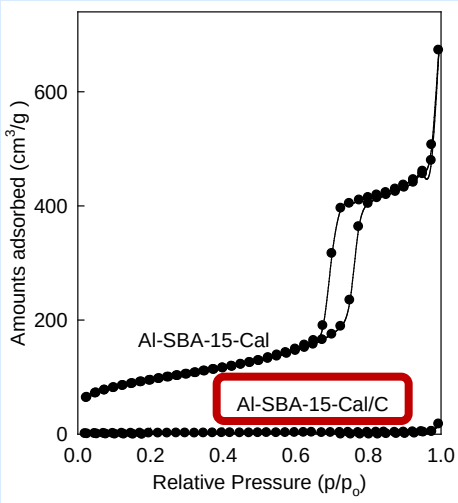
1500 ton multi-anvil (left), multi-anvil assembly (middle), and piston cylinder apparatus (right) used for the synthesis of periodic mesoprous silica materials.

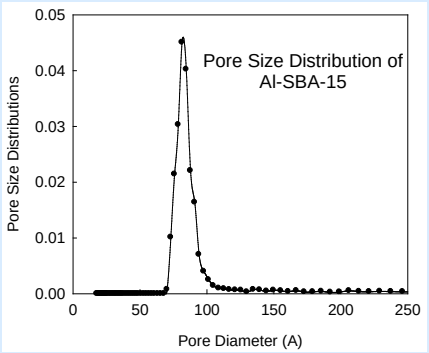
Synthesis of Periodic Mesoporous Aluminosilica with Crystalline Channel Walls

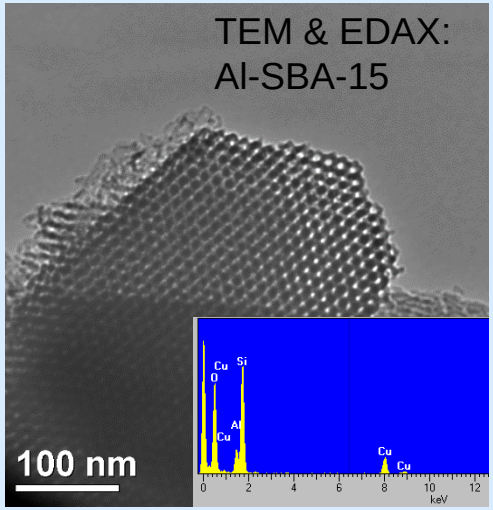


Co-condensation followed by pH adjustment:
Material of Choice: Al-SBA-15
TEOS : $Al_2(SO_4)_3.18H_2O$ = 100-X : X
X=25 wt% of total TEOS wt followed by pH ~ 7.5 adjusted

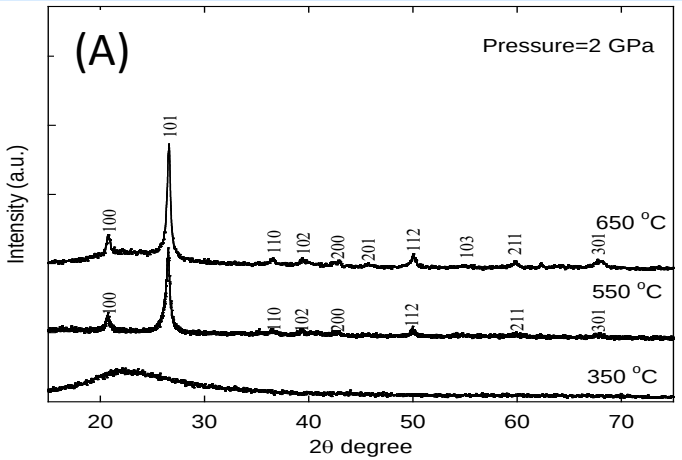
Kresge, C. T. et. al. *Nature* **1992,** *359*, 710;
Xiao et. al. *Chem. Mater.* **2004,** *24*, 7500.

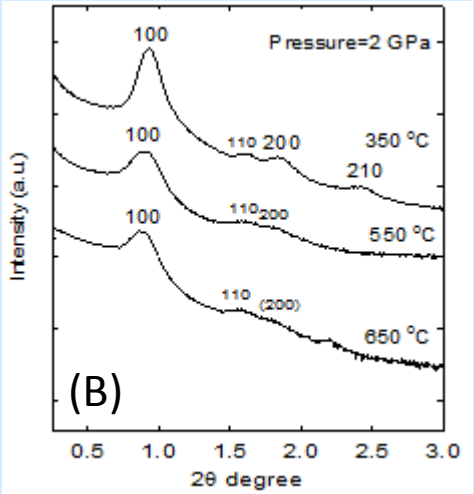


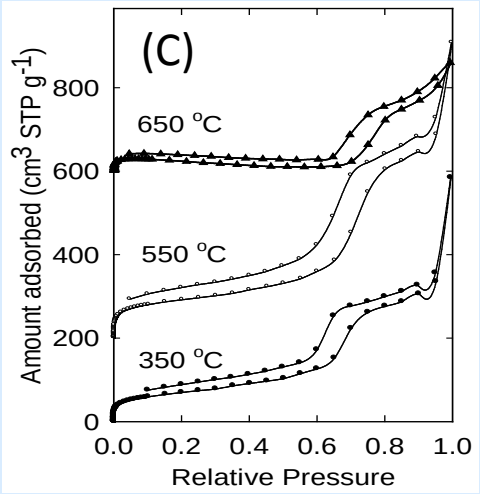


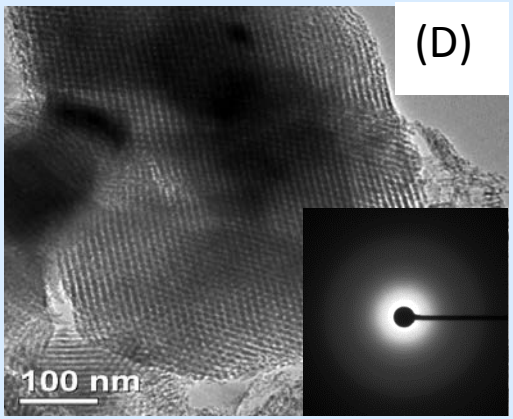


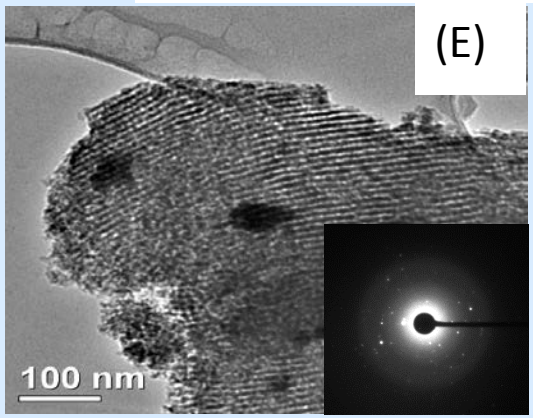
High-pressure Treatments with Al-SBA-15:

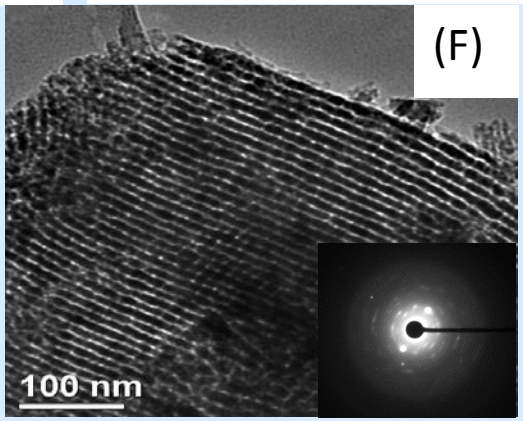






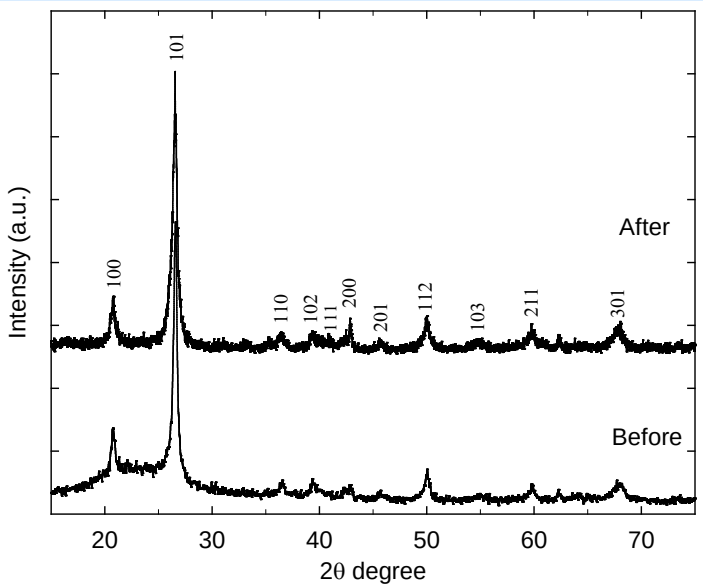


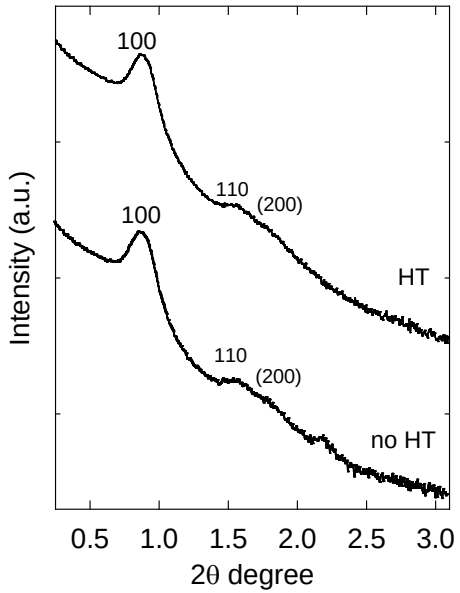


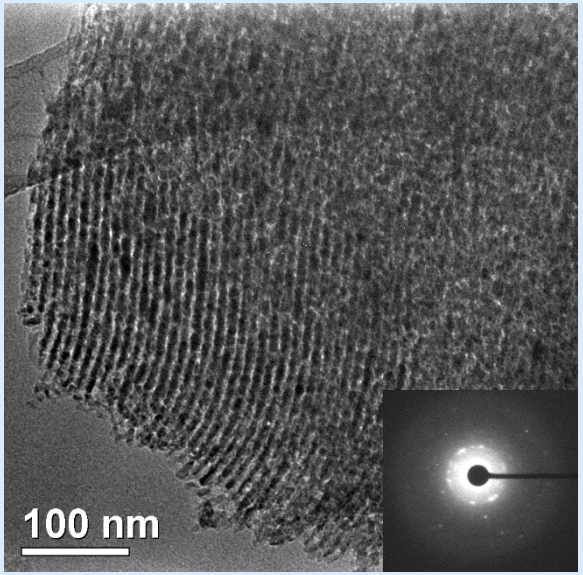


A) XRD patterns; B) SAXS patterns; and C) N_2 adsorption isotherms for the calcined alumina silica/carbon composites treated at 2 GPa and different temperatures for 6h. TEM images for calcined aluminosilica treated at 2 GPa and (D) 350 °C, (E) 550 °C, and (F) 650 °C for 6 h (inset corresponding SAED).

Hydrothermal Stability Study

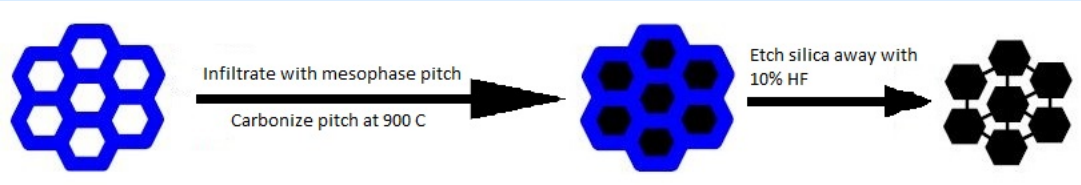


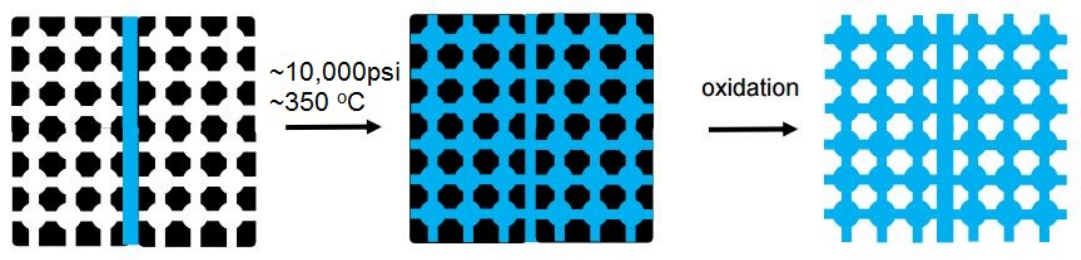




XRD(left) and SAXS(middle) patterns for crystalline aluminosilica synthesized at 2 GPa and 650 ^{o}C before and after treatment in pure steam at 800 ^{o}C for 2 hours. TEM(right) image for the material after treatment.

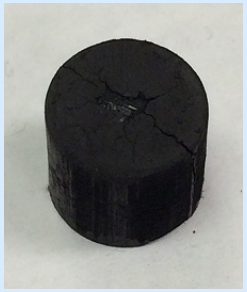
Hydrothermal Growth of Single Crystalline Mesoporous Quartz

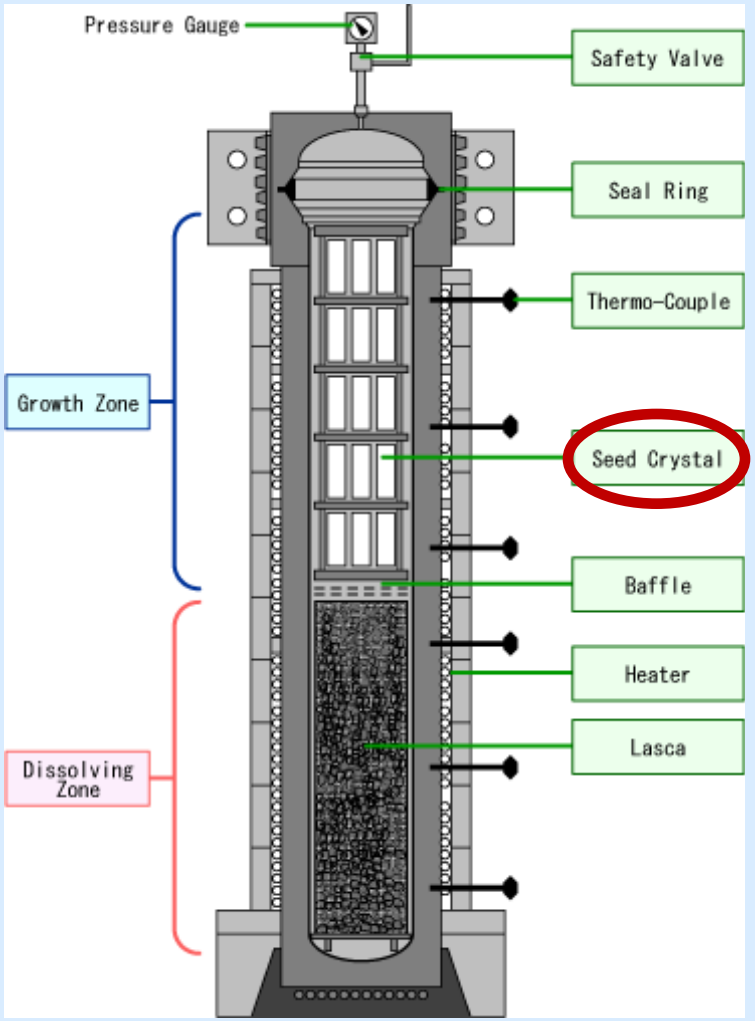




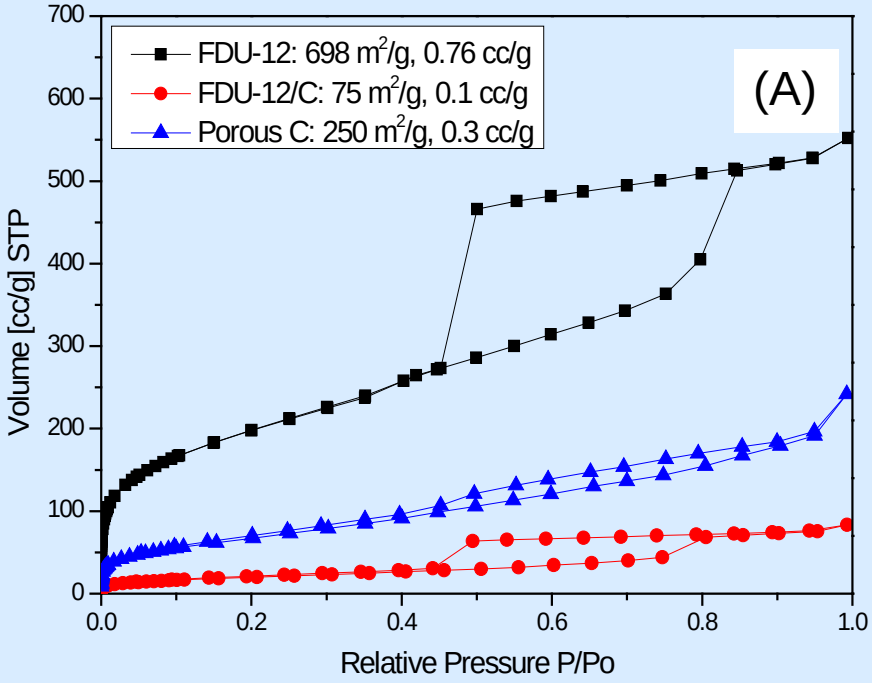
Motivation:

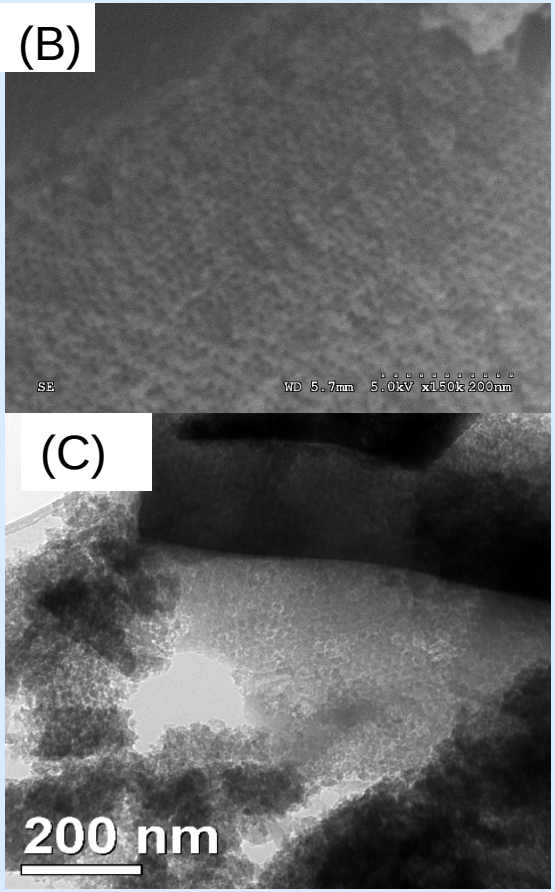
1. Could be applied to practical scale production.
2. Mesoporous quartz single crystal remains unknown.
3. The quartz produced would have the same pore structure as initial silica template.
4. Could add heteroatoms in the growth.

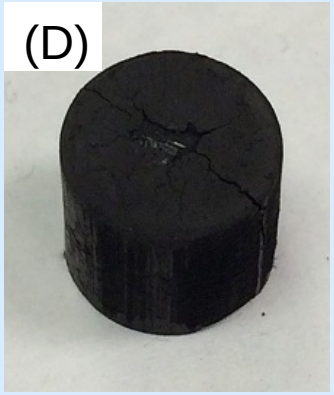




Preliminary Results





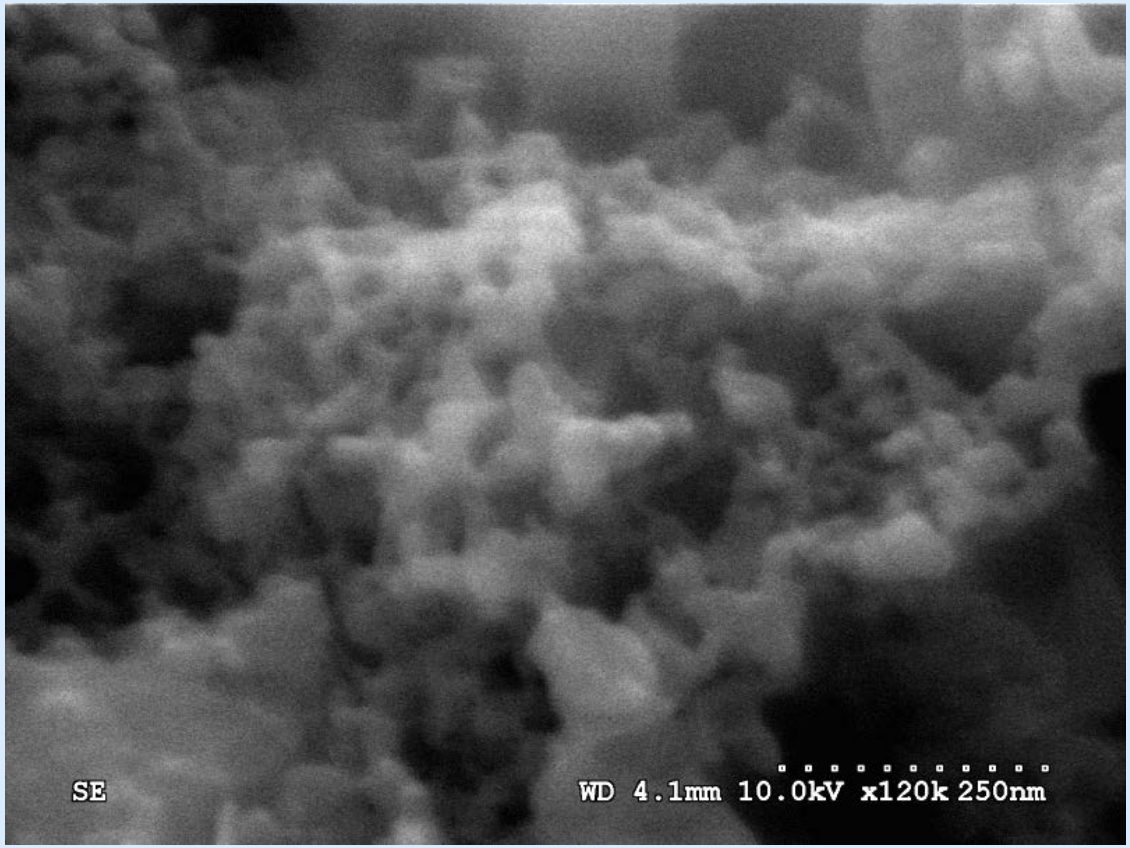


A) N_2 isotherms; B) SEM image of FDU-12; C) TEM image of porous carbon after etching away silica using 10% HF; D) Monolith with quartz seed plate.

Preliminary Results

Temperature used: T_{bott} = T_{diss} = 375 C, T_{grow} = 350 C.
Growth time: 5 days.

Mass of quartz seed plate:
Before: 49.4 mg.
After: 56.8 mg.
Growth: 7.4 mg (15% growth)



SEM image of quartz plate after hydrothermal growth.

Conclusion

1. At a pressure of 2 GPa:

@ 350 ^{o}C, the pore walls composed of aluminosilica remained mostly amorphous;
@ 550 ^{o}C, crystallization of the pore walls;

2. (1) The aluminosilica with crystalline pore walls was found to be steam stable at 800 ^{o}C for at least 2 h with no pore shrinkage.
(2)Aluminium was successfully introduced to the silica network.

These two reasons make the material potentially catalytically active in petroleum cracking.

3. For the growth of quartz single crystal, we have seen some growth, as well as some mesopores. And more experiments are ongoing.

Acknowledgement

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