Accelerating molecular diffusion by constructing hierarchical Murray zeolites for maximized catalytic activity

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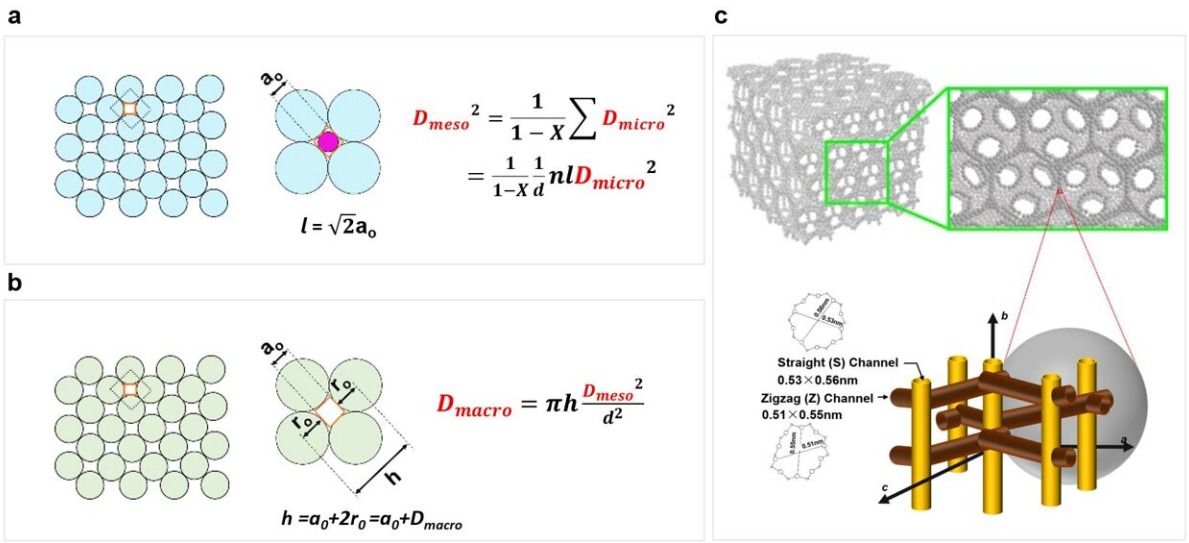


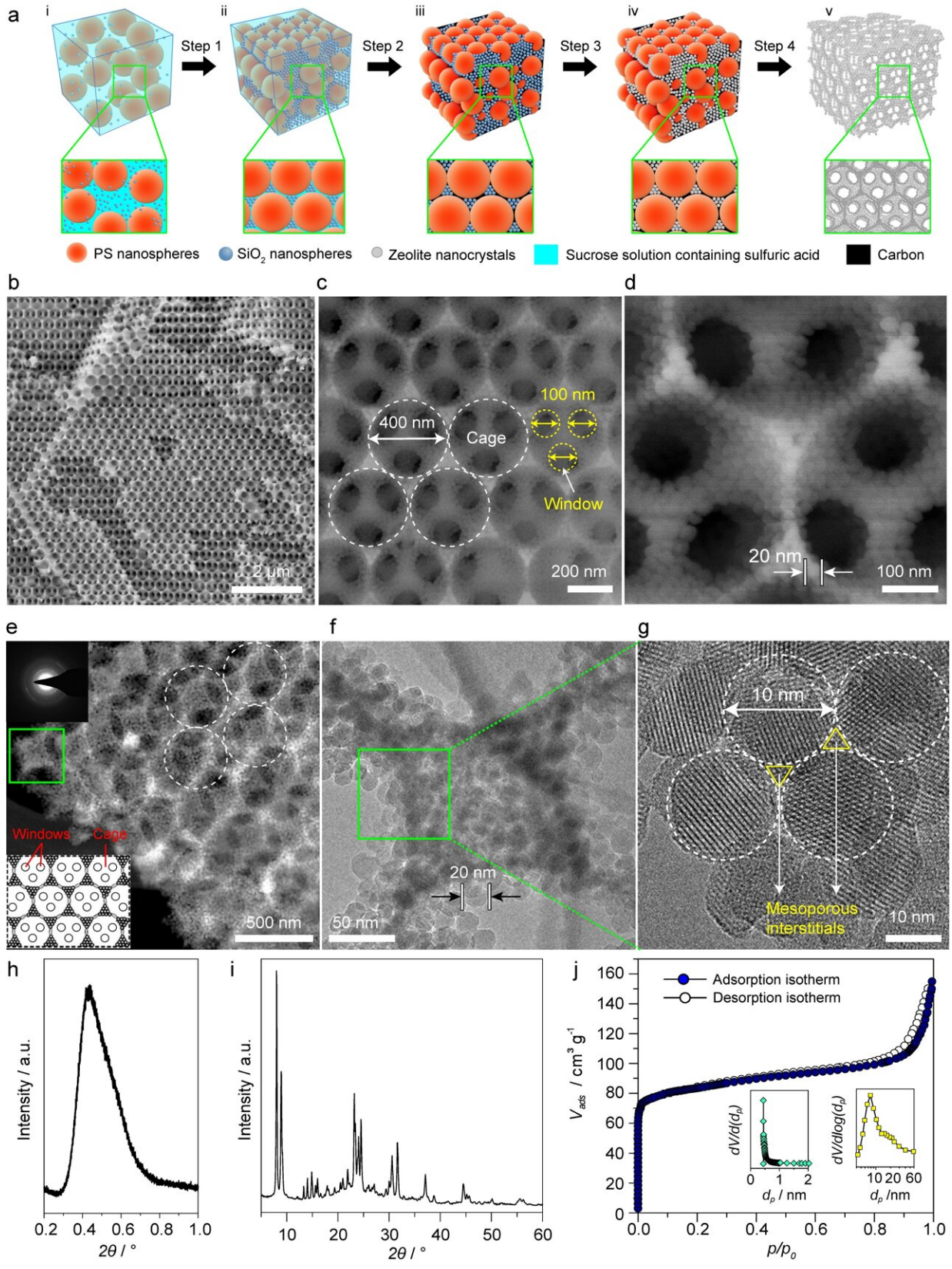
The different size ratios between multi-scale pores based on the generalized Murray's Law. (a) The size ratio between mesopore and micropore. (b) The size ratio between macropore and mesopore and (c) The hierarchically porous structural illustration of OMMM–ZSM-5 zeolites. Credit: Science China Press

Introducing interconnected mesopores and macropores into microporous zeolites with the rationalized pore size at each level is an effective strategy to suppress the diffusion limitations, but remains highly challenging due to the lack of rational design principles.

Guided by the generalized Murray's Law, for the first time, researchers demonstrated the first example of boosting molecular diffusion by constructing hierarchical Murray zeolites (OMMM-ZSM-5) with highly ordered and fully interconnected macro-meso-microporous structure assembled by uniform zeolite nanocrystals. The walls of macropores are constructed from the assembly of highly uniform zeolite nanocrystals, which leads to the formation of an interconnected ordered mesoporous system.

The excellent interconnectivity of hierarchical Murray structure was confirmed by the temperature-dependent hyperpolarized ^{129}Xe nuclear magnetic resonance. Concerning the mass transfer of bulky molecules within the highly interconnected hierarchical Murray structure of OMMM-ZSM-5, the intelligent gravimetric analysis (IGA), a macroscopic diffusion measurement, on the diffusion of 1,3,5-trimethylbenzene, was performed under inert conditions.

OMMM-ZSM-5 zeolites exhibited 9.4 times larger max adsorption amounts and 9 times faster relative diffusion rate than those of conventional ZSM-5 zeolite. Regarding the intracrystalline diffusion behavior and the impact of the interconnected and rationalized macro-meso-micropores in accelerating diffusion in OMMM-ZSM-5 zeolite, the ^{1}H pulsed field gradient (PFG) NMR, a microscopic diffusion measurement, was applied.


a
i
ii
iii
iv
v
Step 1
Step 2
Step 3
Step 4
PS nanospheres
SiO2 nanospheres
Zeolite nanocrystals
Sucrose solution containing sulfuric acid
Carbon
b
2 μm
c
400 nm
Cage
100 nm
Window
200 nm
d
20 nm
100 nm
e
Windows
Cage
500 nm
f
20 nm
50 nm
g
10 nm
Mesoporous interstitials
10 nm
h
Intensity / a.u.
2θ / °
i
Intensity / a.u.
2θ / °
j
Adsorption isotherm
Desorption isotherm
V_ads / cm3 g-1
p/p0
dV/d(dp)
dp / nm
dV/dlog(dp)
dp /nm

(a) Schematic of the synthesis of hierarchically ordered macro–meso–microporous zeolite ZSM-5 (OMMM–ZSM-5) assembled by zeolite nanocrystals. (b)–(j) Characterizations of OMMM–ZSM-5(400), as a representative sample. (b)–(d) SEM images. (e) TEM image and ED pattern (inset). (f) TEM image of enlarged area outlined in (e). (g) HRTEM image of enlarged area outlined in (f). (h) SAXS and (i) WAXS pattern. (j) N2 adsorption–desorption isotherms and micropore-size, mesopore-size distribution (inset). Credit: Science China Press

The total diffusivity of molecules ($D_{f\text{-}intra}$) in the hierarchical Murray zeolite was about 10 times higher than that of microporous zeolite ZSM-5. The above results showed that the interconnected and rationalized macro-meso-micropores in the hierarchical Murray architecture can greatly accelerate the diffusion performance.

Such excellent diffusion property makes hierarchical Murray zeolite ZSM-5 an extraordinary solid acid catalyst in the 1,3,5-triisopropylbenzene 1,3,5-TIPB catalytic cracking. hierarchical Murray zeolite exhibited 2.5 times higher catalytic performance and two times less coke deposition than microporous ZSM-5. It is clear that the presence of excellent hierarchical Murray structural diffusion system provides a highly efficient catalyst, which is promising in many organic catalytic reactions involving large molecules.

The generalized Murray's Law could enable predictable and controlled production of bioinspired hierarchically porous materials with optimized structural features and highly enhanced performance.

The findings are published in the journal *National Science Review*.

More information: Ming-Hui Sun et al, Boosting molecular diffusion following the generalized Murray's Law by constructing hierarchical

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