F. ZHANG, Y. WEI, X. WU, H. JIANG, W. WANG,* H. LI* (SHANGHAI NORMAL UNIVERSITY, P. R. OF CHINA AND UNIVERSITY OF NEW MEXICO, ALBUQUERQUE, USA)

Hollow Zeolitic Imidazolate Framework Nanospheres as Highly Efficient Cooperative Catalysts for [3+3] Cycloaddition Reactions


**A Zeolitic Imidazolate Framework Catalyst for [3+3] Cycloadditions**

**Significance:** The authors developed a hollow-structured zeolitic imidazolate framework (ZIF-8-H) nanosphere as a catalyst for [3+3] cycloadditions. ZIF-8-H was prepared via complexation of carboxylic groups on the surface of nano-PS (ø = 400 nm) with zinc ions and 2-methylimidazole, followed by subsequent removal of the PS nanosphere by extraction with toluene. The reaction of 1,3-dicarbonyl compounds 1 with α,β-unsaturated aldehydes 2 proceeded in the presence of ZIF-8-H to give the pyranyl heterocycles 3 with up to 89.0% conversion and 99.9% selectivity.

**Comment:** The reaction of 1,3-hexanedione and 3-methyl-2-butenal proceeded in the presence of ZIF-8-H with 89.0% conversion, whereas the use of bulk ZIF-8 showed lower catalytic efficiency (73.2% conversion). Toluene vapor adsorption isotherm showed that ZIF-8-H absorbed toluene to a cage-filling level with a high adsorption amount (6.34 mmol/g). Based on this observation, the authors discussed that the limiting aperture size of ZIF-8-H exceeded the kinetic diameter of toluene (0.61 nm), which is much larger than the reported window size of ZIF-8 (0.34 nm).

**Selected examples:**

Selected examples with conversion and selectivity:
- 89.0% conversion, 99.9% selectivity
- 76.7% conversion, 99.9% selectivity
- 65.4% conversion, 99.9% selectivity
- 76.7% conversion, 99.9% selectivity
- 47.5% conversion, 99.9% selectivity