

Tailoring Selectivity With Confinement-Governed Transition States

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Catalytic reactions under steric confinement mimic enzymes and benefit from the proximity of the catalyst to a pore wall with a defined geometry and polarity, thereby offering access to tailored selectivities, productivities, and activities. Here, the concepts of tailoring transition states of catalytic reactions with organometallic catalysts by confinement are presented. The concept was successfully used in the size-specific macrocyclization by tethered and surface-bound neutral ruthenium and cationic molybdenum and tungsten imido alkylidene *N*-heterocyclic carbene (NHC) complexes,^[1-5] in *Z*-selective ring-opening cross-metathesis reactions,^[6] in *Z*-selective hydrosilylation and hydroboration reactions of alkynes by Rh-NHC complexes,^[7] in the alkene-selective oligomerization of ethylene with Cr(II) and Cr(III) complexes as well as in the ring-expansion metathesis polymerization with cationic molybdenum alkylidyne NHC complexes to yield low-molecular weight cyclic polymers^[8]. Also, the concept of liquid confinement in biphasic supported ionic liquid phase (SILP) conditions^[9] will be outlined.

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