

Influence of Restricted Diffusion on Pyrolysis Pathways for Diarylmethanes

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Diarylmethanes serve as models for analogous thermally robust linkages present in various fuel materials. These structures can potentially lead to PAH formation via a free radical cyclization pathway. We have prepared silica-immobilized forms of diphenylmethane ($\text{SiOC}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_5$) and phenyl naphthyl methane ($\text{SiOC}_6\text{H}_4\text{CH}_2\text{C}_{10}\text{H}_7$) to investigate the influence of restricted mass transport on this cyclization pathway. Low conversion studies at 425-450°C indicate that the cyclization pathway is the dominant thermolysis pathway, which generates fluorene and benzofluorene products, respectively. However, restricted diffusion also leads to a competitive radical displacement pathway, involving diarylmethyl radicals, which produces significant quantities of cross-linked triarylmethanes (ca. 8-10 mol %). The selectivity of these pyrolysis pathways as a function of model structure, and the influence of neighboring hydroaromatic spacer molecules on the surface will be reported.

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