The Consequences of Surface Confinement on Free Radical Chemistry

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ABSTRACT

Mass transport limitations impact the thermochemical processing of fossil and renewable energy resources, which involves the breakdown of cross-linked, macromolecular networks. To Investigate the molecular level details of the consequences of molecular confinement on high temperature (275-500°C) free-radical reaction pathways, we have been examining the pyrolysis of model compounds attached to the surface of non-porous silica nanoparticles through a thermally robust Si-O-C_{sp^3} tether. Pyrolysis of silica-immobilized diphenylalkanes and related ethers have been studied in detail and compared with the corresponding behavior in fluid phases. The diffusional constraints can lead to reduced rates of radical termination on the surface, and enhancement of neophyl-like rearrangements, cyclization-dehydrogenation pathways, and *ipso*- aromatic substitutions. Furthermore, studies of two-component surfaces have revealed the importance of a radical relay mechanism involving rapid serial hydrogen transfer steps resulting from the molecular pre-organization on the low fractal dimension silica surface. Key findings are reviewed in this paper, and the implications of these results for fuel processing are described.

INTRODUCTION

Pyrolysis forma the basis for many current and envisioned technologically important processes for conversion of fossil and renewable resources into volatile fuels or chemicals. Since many of these resources are highly cross-linked, macromolecular organic materials. concerns over mass transport limitations are often well-founded. The effects of mass transport limitations have been documented in the pyrolysis of coal,[1] kerogen,[2] cellulose,") lignin,[4] biomass,[5] and polymers." Predictive models have been developed for pyrolysis of coal, lignin, and cellulose that explicitly include descriptions of mass transport mechanisms.[1b-d] These

quantitate

in Figure 3 for the case of bibenzyl, this eliminates the formation of a major product (tetraphenylbutanes) found in fluid phases. As a consequence, new pathways emerge in significant quantities such as cyclization-dehydrogenation

hydrogen transfer steps and are promoted by neighbonng molecules that can participate in the radical relay mechanism

Undoubtedly, the efficiency of this pathway also depends on the ability of molecules to become properly aligned for the oriented hydrogen transfer step on the surface. an area that needs to be studied in more detail Orientation effects can lead to regiospecificity in hydrogen transfer steps that impact product selectivities. This is illustrated in the pyrolysis of =DPP where hydrogen abstractton selectivities (Figure I) varied modestly with changes in surface coverage, favoring abstraction From the benzylic methylene farthest from the surface at lower surface coverages. More dramatic effects on product selectivities were found dunng pyrolysis of

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Surface Composition[a]	Coverage (mmol g^{-1})	Rate

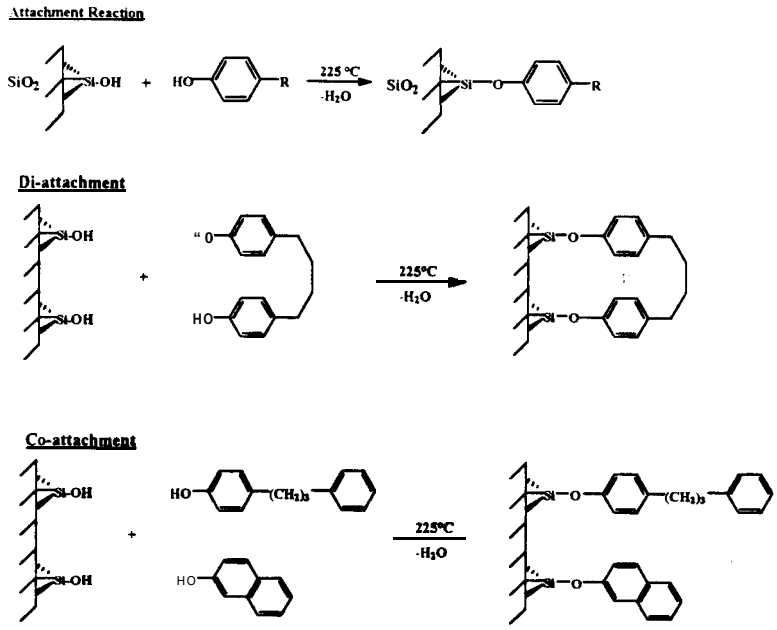

Figure 1. Preparation of silica-immobilized model compounds

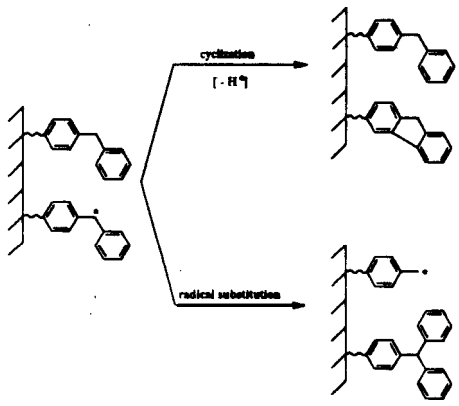

Figure 2. Competing cyclization and radical substitution pathways in pyrolysis of sdica-immobilized diphenylmethane.

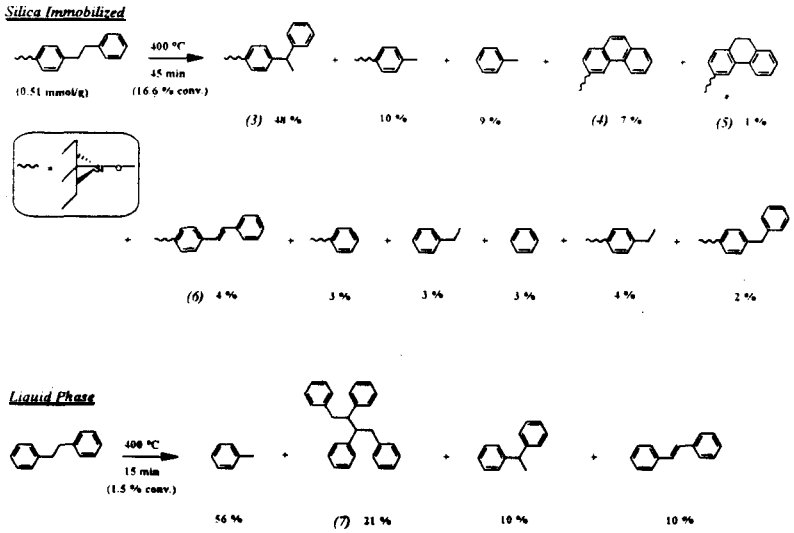

Figure 3. Comparison of pyrolysis products for silica-immobilized and liquid bibenzyl.

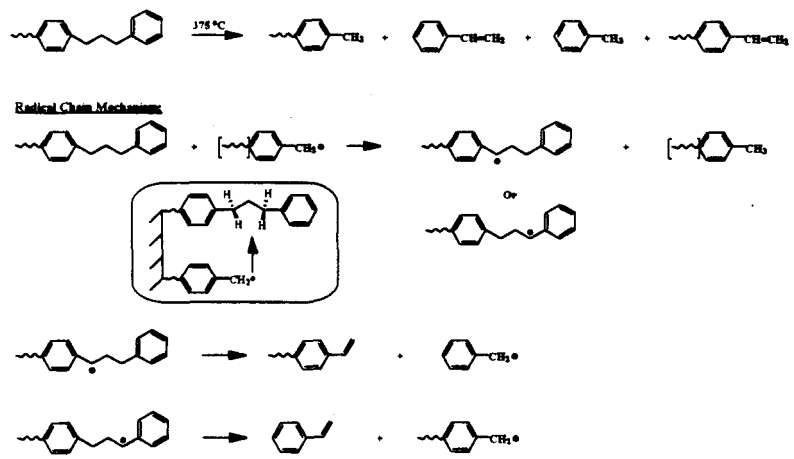

Figure 4. Radical chain propagation steps for the pyrolysis of silica-immobilized 1,3-diphenylpropane. Bracket notation denotes species exists in both gas-phase and surface-attached forms.

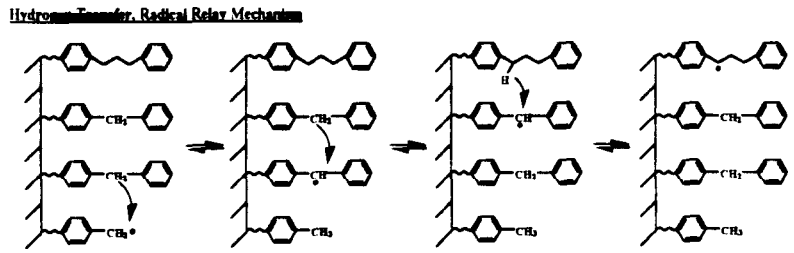

Figure 5. Radical relay mechanism in the pyrolysis of silica-attached 1,3-diphenylpropane.