Confinement effects on product selectivity in the pyrolysis of phenethyl phenyl ether in mesoporous silica

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Pyrolysis of phenethyl phenyl ether confined in mesoporous silicas by covalent grafting results in significantly increased product selectivity compared with fluid phases.

The tailoring of nanoporous silica surfaces by attachment of organic molecules with varying functionality is being widely investigated for applications in many fields such as catalysis, separations, and sensors. Formation of these organic–inorganic hybrid materials can be accomplished directly by co-condensation methods or by chemical grafting following the silica synthesis.[1] Organic molecules are therefore confined in these nanoporous solids, and there is emerging interest in the impact of nanoconfinement on chemical reactivity[2] and its use in organic synthesis[3] and drug delivery.[4]

We have begun exploring confinement effects on high-temperature, free-radical organic reactions through the use of molecules covalently tethered to the pore walls of hexagonal mesoporous silicas, SBA-15 and MCM-41.[5,6] The surface attachment reaction involves the condensation of a phenolic precursor with the silanols to give a silyl aryl ether linkage to the surface as generalized below.

$$\equiv\mathrm{Si{-}OH} + \mathrm{ArOH} \rightarrow \equiv\mathrm{Si{-}O{-}Ar} + \mathrm{H_2O}$$

This linkage is thermally robust permitting the study of reactions under confinement at high temperatures (currently up to *ca.* 375 °C).[5,6] However, the linkage is hydrolytically unstable, which allows the dissolution of the silica support under high pH conditions and the quantitative recovery of all reaction products.

Our studies of the pyrolysis at 375 °C of 1,3-diphenylpropane (DPP) confined in mesoporous silicas over a pore size range of 1.7–5.6 nm revealed that the rate of the free-radical chain reaction is accelerated compared with fluid phases and with DPP attached to a non-porous silica (Cabosil).[5] This effect was attributed to enhanced encounter frequencies in the pores that accelerate key hydrogen transfer steps. For reactions occurring between two spatially confined species, this represents a type of supramolecular catalysis that is of current interest.[7] Confinement also resulted in a modest change in product selectivity (factor of *ca.* 1.2–1.6) indicating that the benzylic hydrogens farthest from the point of surface attachment were more accessible for hydrogen transfer in the pores. Recent studies of benzyl phenyl ether pyrolysis, which occurs by a different free-radical mechanism, showed essentially no influence of pore confinement on product selectivity.[6]

In this paper, we present results for the pyrolysis of phenethyl phenyl ether ($\mathrm{PhCH_2CH_2OPh}$, PPE), a model for the dominant ether linkage in lignin,[8] confined in mesoporous silicas which show substantial alterations in product selectivity upon pore confinement. Pyrolysis of PPE in gas and solution phases has been extensively investigated and the free-radical mechanism is well understood.[8] This chemistry remains operative when PPE is attached to the surface of the non-porous silica Cabosil.[9] The two pairs of reaction products, surface-bound styrene plus gas-phase phenol and surface-bound toluene plus gas-phase benzaldehyde, are shown in Fig. 1. They arise from competing pathways cycling through radicals formed at the α- and β-carbons in PPE. The radical chain propagation steps are shown in Fig. 2. Hydrogen abstraction at the α- methylene by the chain carrying, gas-phase phenoxyl and surface-bound benzyl radicals (eqn (1)) produces the α-benzylic radical that undergoes unimolecular scission (eqn (2)). Competitive abstraction at the β-methylene results in a radical that undergoes an intermediate rearrangement *via* an O–C phenyl shift prior to scission and product formation (eqn (3)). The product selectivity for these two pathways, defined as α/β, is 3.1 ± 0.3 at 375 °C in fluid phases, and a detailed kinetic analysis of this selectivity has been presented.[8] When PPE is attached to the Cabosil surface, the pyrolysis rate (375 °C) was unchanged and the

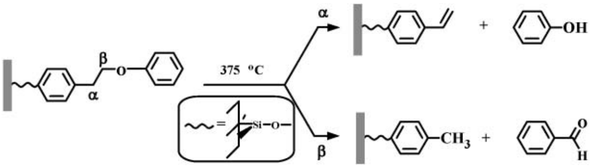

Fig. 1 Products from pyrolysis of silica-immobilized PPE.

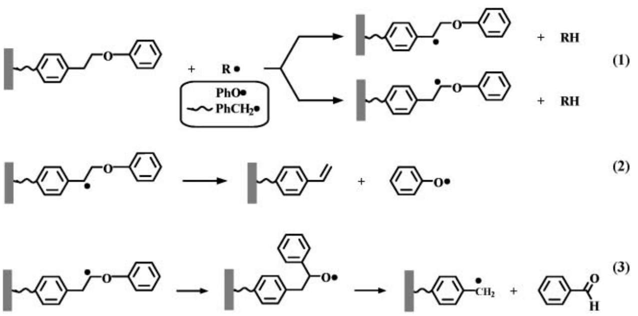

Fig. 2 Propagation steps in the free-radical chain reaction of silica-immobilized PPE.

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Table 1 PPE pyrolysis data at saturation grafting density and 375 °C

Silica[a]	Pore size[b]/nm	PPE density[c]/nm^{-2}	Reaction rate[d] (% h^{-1})	Path selectivity[e] (α/β)
Cabosil (200 m^2 g^{-1})	n.a.	1.82	8.3[f]	5.0 ± 0.8[f]
SBA-15 (833 m^2 g^{-1})	5.8	0.74	13.9	14.2 ± 0.6
MCM-41 (1058 m^2 g^{-1})	2.5	1.21	14.4	13.3 ± 1.5
MCM-41 (1183 m^2 g^{-1})	2.0	1.15	14.2	17.5 ± 2.1

[a] Silica support with specific surface area from BET nitrogen adsorption isotherm. [b] BJH mean pore diameter calculated from the adsorption branch. [c] PPE grafting density (molecules nm^{-2} surface area) corrected for the mass of the organic. [d] Initial rate of PPE conversion measured from the slope of a plot of PPE conversion *vs.* reaction time. Error is ±5–10%. [e] α/β-path selectivity based on product yields (see Fig. 1 and 2). Values are averages of 5–8 pyrolyses. [f] From Britt *et al.*[9] The corresponding selectivity for fluid-phase PPE is 3.1 ± 0.3.[8]

α/β-selectivity increased slightly to 5.0 ± 0.8. This increase was attributed primarily to a small substituent effect from the *para*-silyloxy tether to the surface that provides additional stabilization to the α-benzylic radical formed competitively in eqn (1).

PPE was grafted at saturation density to three mesoporous silicas with pore diameters of 2.0–5.8 nm as shown in Table 1.† The saturation grafting densities in the MCM-41s are comparable to those measured previously for DPP in analogous materials, which is consistent with the similarity in molecular size and grafting orientation (*para*-linkage to the surface) for the two molecules.[5] The PPE grafting density in SBA-15 is smaller than in the MCM-41s, despite the larger pore size, because of the considerable amount of surface area that is largely inaccessible in interconnecting micropores.[5,10]

Pyrolysis of the mesoporous silica-confined PPE was carried out at 375 °C, which generated the same products shown in Fig. 1.† The reaction rates and α/β-selectivities are collected in Table 1 along with the values obtained previously on Cabosil. The pyrolysis rate is accelerated in the mesoporous silicas as observed previously for DPP,[5] but we do not have Cabosil data at similar PPE grafting densities to make an exact comparison. However, the most striking effect is the substantial increase in product selectivity indicated by the α/β-selectivity values that are a factor of three larger than for Cabosil. This enhancement in selectivity does not appear to have a measurable dependence on the pore size in the range studied. Since pore confinement should have little effect on the selectivity for hydrogen abstraction at the α- and β-sites (Fig. 1, eqn (1)), our interpretation is that confinement in the pore leads to a more congested environment that hinders the critical O–C phenyl shift step in eqn (3) (Fig. 2). A decreased rate for this path would allow β-radicals to interconvert by hydrogen transfer to form the thermochemically favored α-benzylic radicals, hence increasing the α/β-selectivity.

Table 2 Effect of grafting density and tethered biphenyl spacer on PPE pyrolysis in SBA-15 at 375 °C

Surface composition[a]	Grafting density[b]/nm^{-2}	Reaction rate[b] (% h^{-1})	Path selectivity[b,c] (α/β)
PPE	0.74	13.9	14.2 ± 0.6
PPE	0.28	15.9	25.7 ± 1.8
PPE/BP	0.22/0.64	11.8	43.6 ± 1.6

[a] PPE = phenethyl phenyl ether; BP = biphenyl. [b] See Table 1 for definitions. [c] The selectivity for fluid-phase PPE is 3.1 ± 0.3, which is independent of concentration in biphenyl diluent.[8]

To see if changing the PPE grafting density might have an impact on the α/β-selectivity, PPE was grafted into SBA-15 at 0.28 nm^{-2}, which is 38% of the saturation coverage (Table 2). Surprisingly, the α/β-selectivity increases to a value of *ca.* 26 despite what might appear to be a less crowded environment in the pore resulting from the lower grafting density. One possible explanation for this behavior is that, at the lower PPE surface density, the molecules are interacting more strongly with the silica surface which sterically hinders the O–C phenyl shift. It has been shown, for example, that silica surfaces can inhibit the rate of a related 1,2-phenyl shift (C–C) for the neophyl radical rearrangement during thermolysis of β-phenylisovaleryl peroxide adsorbed on silica gel.[11]

$$\mathrm{PhC(CH_3)_2CH_2\cdot \rightarrow \cdot C(CH_3)_2CH_2Ph}$$

This conclusion is also supported by molecular dynamics (MD) simulations that utilize a recently developed model of hexagonal mesoporous silica that has also been used for hybrid materials containing tethered organic molecules.[12] Fig. 3 displays representative structures from MD simulations (375 °C; 100 ps) for PPE grafted into a 2.9 nm diameter pore at 42% of saturation density (top) and at saturation density (bottom). For the saturation

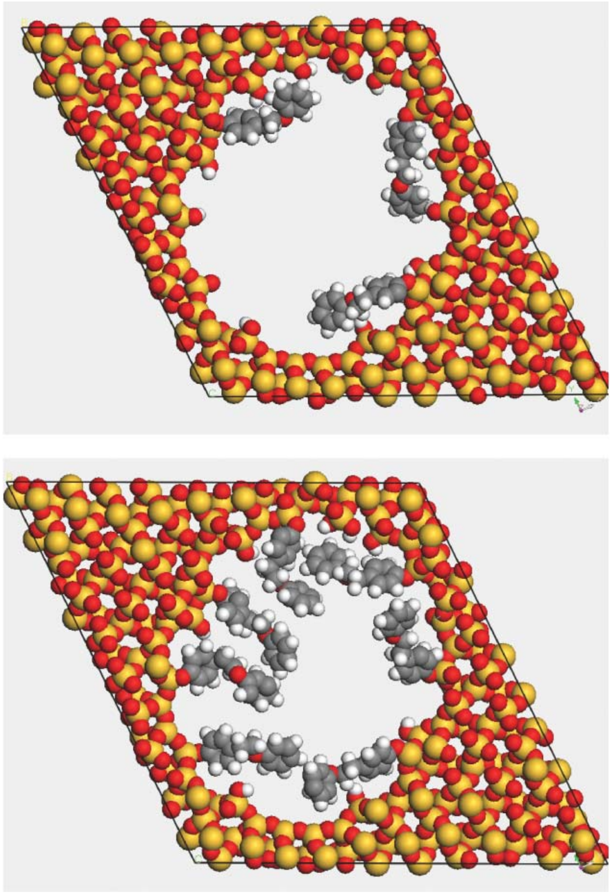

Fig. 3 Models for hexagonal mesoporous silica (2.9 nm pore diameter) containing tethered PPE molecules at densities of 0.57 nm^{-2} (top) and 1.33 nm^{-2} (bottom). Yellow, silicon; red, oxygen; grey, carbon; white, hydrogen.

coverage, the same lowest energy configuration for seven tethered molecules previously found for DPP was employed as the starting point.[5] The lower PPE grafting density mimics the same reduction in grafting density (38% of saturation) used in the SBA-15 pyrolysis studies (Table 2). The key result is that at the low grafting density, PPE molecules spend most of their time interacting with the surface, whereas at saturation coverage this is not possible and a fraction of the molecules are always extended into the pore volume. Interestingly, the simulations show that hydrogen bonding interactions between the PPE ether oxygen and underivatized surface silanols are particularly prevalent at low grafting densities, and this will be the subject of future detailed investigation.

Finally, we explored whether the PPE pyrolysis selectivity could be altered by controlling the nanoscale structure of the organic-inorganic interface. In prior studies on Cabosil, we showed that reaction rates and product selectivities for free-radical reactions can sometimes be altered by both the structure and grafting orientation of a second "spacer" molecule on the surface,[13] and aromatic spacers were found to increase the selectivity for PPE.[9] In the current study, a two-component material on SBA-15 was prepared containing PPE in the presence of only a three-fold excess of grafted biphenyl (BP) molecules (Table 2). Pyrolysis of this material results in an even larger increase in the PPE α/β-selectivity to *ca.* 44 suggesting that the rearrangement path is more hindered in the presence of the rigid BP spacer molecules on the surface. The impact of the grafted BP "surface solvent" is unique to this restricted mass transport setting, since in fluid phases the α/β-selectivity is independent of PPE concentration when diluted in BP.[8]

This research provides clear evidence for a reaction whose product selectivity can be substantially altered by pore confinement, grafting density, and tailoring the interfacial environment with spacer molecules. For PPE pyrolysis, the path selectivity could be changed by over an order of magnitude (3.1 to 43.6) compared with the inherent fluid-phase selectivity. Additional research is planned to explore in detail the effects of structure and grafting density of spacer molecules, grafting orientation of PPE molecules, and pore size on this reaction. This research also contributes to the growing field of research investigating organic radical transformations on solid supports.[16]

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Notes and references

† MCM-41[14] and SBA-15[15] silicas were prepared according to published procedures. Preparation of the mesoporous silica-confined PPE utilized the same methods described for DPP.[5] Briefly, saturation coverages were prepared by the condensation of *p*-hydroxyphenethyl phenyl ether (2.8 g, 13.0 mmol) with the silanols of the mesoporous silica (1.0 g, *ca.* 5 mmol SiOH) that had been dried in an oven (200 °C, 4 h). The reaction took place at 225 °C for 1 h in a sealed tube under vacuum (2×10^{-6}) Torr. Unreacted phenol was removed by vacuum sublimation (225–275 °C)[5] followed by extraction (5 × 30 mL) with dry methylene chloride. The solid was dried in a vacuum oven (95 °C, 5 mm Hg) overnight and then stored in a vacuum dessicator. Determination of PPE grafting densities was based on two methods, quantitative analysis by GC following an aqueous base hydrolysis procedure and by carbon elemental analysis,[5] which gave values that agreed within ±3%. Low coverage PPE on SBA-15 was prepared by limiting the amount of precursor phenol (0.90 g, 4.2 mmol) relative to the silica (1.0 g). The two-component sample of PPE/BP on SBA-15 was prepared by first making a saturation coverage of BP and then exchanging PPE on to the surface in a second step. Pyrolysis experiments (5–8 per sample; 50–70 mg each) were conducted in sealed T-shaped tubes under vacuum (2×10^{-6} Torr) as described previously.[5] The gas-phase products were collected in a cold trap and analyzed by GC and GC-MS with internal standards. Surface-attached products were analyzed similarly following base hydrolysis of the solid residue which liberates these products as the corresponding phenols.[5] Mass balances were quantitative to ±3%.

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