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Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

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Abstract

Mass transport limitations impact the thermochemical and catalytic processing of fossil and renewable resources into desirable products. We have been examining the fundamental aspects of restricted mass transport on high temperature, free-radical reactions for model compounds that are covalently attached to the surface of nonporous silica nanoparticles (Cabosil). In the current investigation, we examine the impact of pore confinement on the pyrolysis (375°C) kinetics and product distribution for 1,3-diphenylpropane (DPP) attached to high surface area, mesoporous silicas, SBA-15 and MCM-41, whose pore sizes can be controlled. Reaction of the surface silanols of the mesoporous silicas with *p*-(3-phenylpropyl)phenol gave the corresponding surface-attached (Si-O-C_{aryl} linkage) DPP, which has been characterized by BET surface analysis, elemental and chemical analysis, FTIR and NMR. Initial pyrolysis results indicate that the rate and product distribution depend on the pore size of the mesoporous silica (1.9-5.6 nm). The DPP pyrolysis behavior will also be compared with that in the gas phase and on the nonporous silica.

Extended Abstract

Our research on the effects of restricted mass transport on the pyrolysis kinetics and mechanisms of fuel model compounds has employed molecules chemically attached to the surface of fumed silica particles.¹⁻³ These silica nanoparticles are nonporous and derive their moderately high surface areas (200 m² g⁻¹) from the small particle size (12 nm). Hence, the molecules are all attached on the external surface of the relatively flat, low fractal dimension (2.08) silica in essentially a two-dimensional confinement. The chemistry and spectroscopy of molecules and reactive intermediates, like free radicals, confined in the pores of zeolites and other porous solids continue to be heavily investigated.⁴⁻⁷ For example, a samarium (II) catalyst was recently grafted in a 3.3 nm pore diameter MCM-41 silica, which was then used to reduce fluorenone selectively to the corresponding alcohol without the formation of the dimeric pinacol product.⁷ This result was attributed to reduced rates for bimolecular radical coupling reactions as a consequence of the surface confinement, consistent with our observations on radical reactions in the pyrolysis of fuel model compounds on fumed silica. This topic of pore confinement also has relevance to the thermochemical conversion of organic energy resources, such as coal, which are also porous media. Mass transport limitations in the processing of non-softening coals have been attributed to hindered tar transport between pores.¹ Hence, we are now extending our fundamental pyrolysis studies to investigate the effects of pore confinement on pyrolysis mechanisms, and our initial results on 1,3-diphenylpropane are described below.

Experimental Section

Materials. Benzene was distilled from sodium before use. High purity acetone, dichloromethane, 1,1,3,3-tetramethyldisilazane and water were commercially available and used as received. Cumene was fractionally distilled (2x), and 2, 5-dimethylphenol and *p*-phenylphenol were recrystallized (3x) from hexanes and benzene/hexanes, respectively, prior to use. The synthesis and purification of *p*-HOC₆H₄(CH₂)₃C₆H₅ has been described in a previous paper.³ Cabosil was commercially available (Cabot Corp.). The mesoporous silica, SBA-15, was prepared following standard procedures employing the EO₂₀PO₇₀EO₂₀ amphiphilic triblock copolymer as template and reaction temperatures of 35 °C for 20 hours and then 80 °C for 48 hours. MCM-41 was synthesized by standard methods using hexadecyltrimethylammonium bromide as the template. Resulting pore sizes and surface areas are given in Table 1.

Surface Attachment. Surface attachment procedures are followed according to a previously established method, and only highlights are given below. Excess *p*-(3-phenylpropyl)phenol (HODPP) is adsorbed onto the surface of the dried silica by solvent evaporation from a benzene slurry. The attachment reaction was performed at 225 °C for 1 hour, in a fluidized sand bath on a thoroughly degassed, evacuated (< 10⁻⁵ Torr), sealed sample. The sample was then transferred to another tube, connected to a vacuum at 5 x 10⁻³ Torr, and heated in a tube furnace from 225 to 275 °C at a rate of 10 °C/ 10 min. and held at 275 °C for 10 minutes, to remove unreacted HODPP. The samples were stored in a desiccator under vacuum. Surface coverage analysis was determined via the base hydrolysis procedure described below, and by carbon elemental analysis (Galbraith Laboratories).

Silylation of Cabosil, SBA-15 and MCM-41. The silylation reactions were performed according to the procedure of Anwender, et. al.⁹ The silica was dried at 200 °C for 4 hours and cooled in a desiccator. Approximately 0.1 – 0.2 g of the dehydrated material was suspended in ca. 10 mL of *n*-hexane. 1,1,3,3-Tetramethyldisilazane (5mmol) diluted in 5mL *n*-hexane, was added to the silica slurry and stirred at ambient temperature for 24 hours. The unreacted disilazane was separated by filtration on a 30 mL fine fritted filter (30F), followed by several additional washings with *n*-hexane. The solid material was dried under vacuum for 5 hours at room temperature, then heated to 250 °C for 3 hours under high vacuum. Surface coverage analysis was performed by carbon elemental analysis.

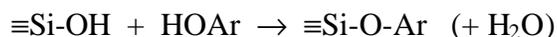
Surface and pore analysis. The surface analysis based on the nitrogen adsorption and desorption isotherm at 77 K was performed on a Quantachrome AUTOSORB-1 system. The BET specific surface area was obtained from the nitrogen adsorption data in the relative pressure range from 0.05 to 0.35. The pore size data was analyzed by the BJH (Barrett-Joyner-Halenda) method from an analysis of the desorption branch of the isotherm.

Thermolysis Procedure. A weighed amount of sample (0.03-0.09 g) was placed in one end of a thoroughly cleaned T-shaped Pyrex tube, evacuated, and sealed at ca. 2 x 10⁻⁶ Torr. The sample was inserted into a preheated temperature-controlled tube furnace (±1°C) fitted with a copper sample holder, and the other end was placed in a liquid nitrogen bath. The products that evolved were collected in the cold trap and dissolved in acetone (0.1-0.2 mL) along with 0.1mL each of the internal standards, cumene, and 2, 5-dimethylphenol, and *p*-phenylphenol. These products were analyzed by GC on a Hewlett-Packard 5890 Series II gas chromatograph employing a J & W Scientific 30 m x 0.25 mm i.d. DB-1 bonded-phase methylsilicone capillary column and flame-ionization detection. GC-MS spectra were obtained at 70 eV with a Hewlett-Packard 5890 Series II gas chromatograph-mass spectrometer equipped with a capillary column matched to that used for GC analyses. The surface-attached products were analyzed through base hydrolysis of the solid residue, addition of 2,5-dimethylphenol (0.1 mL) and *p*-phenylphenol (1.0 mL) as internal standards, acidification of the solution with HCl, and extraction with dichloromethane. The solvent was evaporated and the residue was silylated with BSTFA:Pyridine (1:2) and analyzed via GC and GC-MS.

Results and Discussion

Surface Chemistry. Semicrystalline, mesoporous silicas MCM-41 and SBA-15 contain hexagonally arranged mesopores of controllable size that can be readily functionalized with organic and organometallic moieties.⁸ Applications range from chemical separations to catalysis. Most surface derivatization schemes involve the reaction of a silane coupling agent (R_3Si-Cl , R_3Si-OR' , $R_3Si-NH-SiR_3$) with the surface silanols to give a siloxane linkage ($\equiv Si-O-SiR_3$) to the surface. The silazane, $Me_2HSi-N-SiHMe_2$, has been used to report the density of accessible silanol sites for MCM-41.⁹ In Table 1, quantitative silylation results for this reagent reacting with Cabosil, SBA-15 (5.6 nm), and MCM-41 (2.9 nm) are compared. Our value for the density of accessible surface silanols for MCM-41 (1.99 nm^{-2}) compares favorably with that obtained by Anwender for a MCM-41 with a slightly higher surface area of $1139 \text{ m}^2/\text{g}$ (1.85 nm^{-2}). Note that similar densities of surface silanols are obtained for silylated Cabosil and SBA-15.

In our studies of the pyrolysis of immobilized fuel model compounds on the surface of Cabosil, we have employed a different surface derivatization method that does not employ silane coupling reagents. The reaction of the surface silanols with a phenolic precursor results in a $Si-O-C_{aryl}$ linkage to the surface. We have found this linkage to be thermally robust to ca. $550 \text{ }^\circ\text{C}$, which permits the study of pyrolysis reactions under surface



confinement. However, the linkage is easily cleaved with aqueous base permitting the recovery of reaction products from the surface. It is anticipated that the maximum surface densities of the larger DPP moieties will be less than for the smaller silane derivative. The three silicas were reacted with excess *p*-HOPh(CH₂)₃Ph and analyzed by both chemical analysis (*vide supra*) and carbon elemental analysis (combustion). The surface coverages for these two methods (Table 1) are in agreement for all three silicas within $\pm 5\%$ indicating that the DPP molecules can be completely recovered from the mesoporous silicas by the chemical method. As expected, the DPP surface densities are lower than the SiHMe₂ densities. However, it is interesting that the magnitude of this effect is larger for the mesoporous solids suggesting a more crowded environment than on the exterior surface of the nonporous Cabosil particles. Additional results from BET surface analysis, FTIR, and NMR relaxation measurements will be given in the presentation.

Table 1. Surface derivatization of silicas with $(Me_2HSi)_2NH$ and *p*-HOPh(CH₂)₃Ph

Surface Analysis	Cabosil (200 m ² /g)	SBA-15 (543 m ² /g; 5.6 nm pore)	MCM-41 (1088 m ² /g; 2.9 nm pore)
---SiH(CH₃)₂			
Coverage (mmol/g) ^a	0.68	1.45	2.97
Density (nm ⁻²) ^c	2.12	1.77	1.99
---Ph(CH₂)₃Ph			
Coverage (mmol/g) ^a	0.55	0.94	1.62
Coverage (mmol/g) ^b	0.53	0.99	1.71
Density (nm ⁻²) ^c	1.78	1.37	1.43
Density Reduction (SiHMe ₂ → DPP)	16 %	23 %	28 %

^a From elemental analysis (carbon) on a per g of derivatized silica basis.

^b From chemical analysis on a per g of derivatized silica basis.

^c Calculated on a per g of silica basis.

Pyrolysis Results. Surface-attached 1,3-diphenylpropane (\approx DPP) undergoes a free radical chain decomposition reaction at 375°C to produce surface-attached toluene and gas-phase styrene plus the complementary product pair, gas-phase toluene and surface-attached styrene as shown in Figure 1. The free radical chain mechanism (chain length in excess of 200) involves hydrogen abstraction by surface-attached and gas-phase benzyl radicals from the benzylic positions of \approx DPP to give the regiochemically distinct benzylic radicals shown in Figure 1. These radicals undergo facile β -scission reactions to produce the surface-attached and gas-phase styrene products, as well as regenerating the chain carrying benzyl radicals. Reaction rates and selectivity in product formation are highly dependent on surface coverage (proximity of neighboring molecules and radicals involved in hydrogen transfer propagation steps). At saturation surface coverages, the \approx DPP pyrolysis rate is comparable to that in fluid phases, but decreases dramatically with decreasing surface coverage. As can be seen from the data in Table 2, \approx DPP pyrolysis rates at saturation surface coverage for the mesoporous silicas, despite the lower density of derivatized sites, are somewhat faster than that for the Cabosil and appear to be faster for the smaller pore size. This suggests that there is a pore-size dependence for the pyrolysis rate, which likely arises from faster hydrogen atom transfer steps on the surface, for the smaller, more highly curved pores. Additional studies of smaller pore size MCM-41 materials (2.0-2.4 nm) are in progress. Since the size of a DPP molecule is approximately 1.2 nm, these pores could become quite crowded and lead to interesting pyrolysis behavior.

Selectivity in product formation, measured by the ratio of styrene to toluene yields in the gas phase, reports on the relative rates of formation of the benzylic radical site farthest from the surface relative to the site nearest the surface (*para*- to the silyloxy surface linkage) as shown in Figure 1. For Cabosil at saturation surface coverages of DPP, the value of 0.95 reported in Table 2 is consistent with a small stabilizing substituent effect of the *p*-silyloxy linkage. As shown in Table 2, this selectivity is 1.00 for the SBA-15 and 1.26 for the MCM-41, suggesting an increasing preference for hydrogen abstraction at the benzylic site farthest from the surface in the pores, which increases in magnitude with decreasing pore size. Confirmation of this hypothesis will again require experiments in MCM-41 materials with smaller pore sizes as planned.

Figure 1. Pyrolysis Products and radical chain propagation steps for surface-attached DPP.

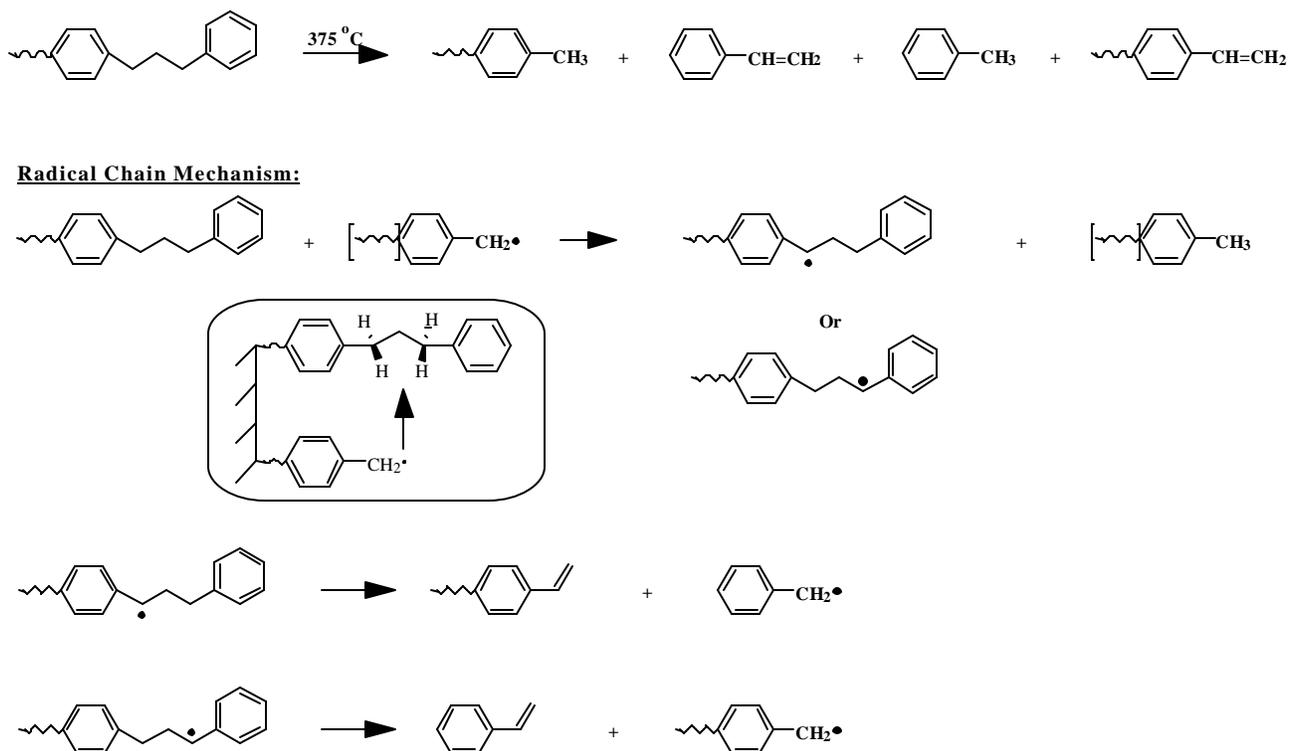


Table 2. Pyrolysis results for surface-immobilized 1,3-diphenylpropane (\approx DPP) at saturation surface coverage.

Silica	Pore Size (nm)	\approx DPP Surface Coverage (mmol/g)	\approx DPP Surface Density (nm^{-2})	\approx DPP Pyrolysis Rate at 375°C ^a (%/h)	Path Selectivity (PhCH=CH ₂ /PhCH ₃)
Cabosil	NA	0.55	1.8	8.4	0.95
SBA-15	5.6	0.99	1.4	11.3	1.00
MCM-41	2.9	1.71	1.4	14.4	1.26

^a Rates are obtained from the slopes of plots of \sim DPP conversion versus time, and have a typical accuracy of \pm 10%.

Conclusions

Mesoporous silicas, SBA-15 and MCM-41, can be derivatized with phenols to give novel hybrid materials possessing thermally robust Si-O-C_{aryl} linkages. Initial pyrolysis results for the surface-attached DPP probe molecule suggest that pore confinement can lead to larger reaction rates and alterations in product selectivity that may correlate with pore size. Additional experiments with smaller pore size MCM-41 silicas are in progress.

Acknowledgment.

This research was sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

References

1. Buchanan, III, A. C.; Britt, P. F. "Investigation of Restricted Mass Transport Effects on Hydrocarbon Pyrolysis Mechanisms," *J. Anal. Appl. Pyrolysis* **2000**, *54*, 129-153; and references therein.
2. Buchanan, III, A. C.; Britt, P. F.; Skeen, J. T.; Struss, J. A.; Elam, C. L. "Pyrolysis of Silica-Immobilized Benzyl Phenyl Ether: Competing Radical Rearrangement Pathways Under Restricted Diffusion," *J. Org. Chem.* **1998**, *63*, 9895-9903.
3. Buchanan, III, A. C.; Britt, P. F.; Thomas, K. B.; Biggs, C. A. "Evidence For a Radical Relay Mechanism During Reaction of Surface-Immobilized Molecules," *J. Am. Chem. Soc.* **1996**, *118*, 2182-2189.
4. Rouhi, A. M. "Boxed In: Chemistry in Confined Spaces," *Chem. & Eng. News* **2000**, August 21, 40.
5. Turro, N. J. "From Boiling Stones to Smart Crystals: Supramolecular and Magnetic Isotope Control of Radical- Radical Reactions in Zeolites," *Acc. Chem. Res.* **2000**, *33*, 637-646.
6. Joy, A.; Uppili, S.; Netherton, M. R.; Scheffer, J. R.; Ramamurthy, V. "Photochemistry of a Tropolone Ether and 2,2-Dimethyl-1-(2H)-naphthalenones within a Zeolite: Enhanced Diastereoselectivity via Confinement," *J. Am. Chem. Soc.* **2000**, *122*, 728-729.
7. Nagl, I; Widenmeyer, M.; Grasser, S.; Kohler, K.; Anwander, R., "Surface-Confined Ketyl Radicals via Samarium (II)-Grafted Mesoporous Silicas," *J. Am. Chem. Soc.* **2000**, *122*, 1544-1545.
8. Anwander, A., "SOMC@PMS: Surface Organometallic Chemistry at Periodic Mesoporous Silica," *Chem. Mater.* **2001**, *13*, 4419-4438.
9. Anwander, R.; Nagl, I; Widenmeyer, M.; Engelhardt, G.; Groeger, O.; Palm, C.; Roser, T., "Surface Characterization and Functionalization of MCM-41 Silicas via Silazane Silylation," *J. Phys. Chem. B* **2000**, *104*, 3532-3544.