

IMPACT OF ORGANIC-MINERAL MATTER INTERACTIONS ON THERMAL REACTION PATHWAYS FOR COAL MODEL COMPOUNDS

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Key Words: Pyrolysis, mineral matter, model compounds

INTRODUCTION

Coal is a complex, heterogeneous solid that includes interdispersed mineral matter. However, knowledge of organic-mineral matter interactions is embryonic, and the impact of these interactions on coal pyrolysis and liquefaction is incomplete.⁽¹⁾ Clay minerals, for example, are known to be effective catalysts for organic reactions.⁽²⁾ Furthermore, clays such as montmorillonite have been proposed to be key catalysts in the thermal alteration of lignin into vitrinite during the coalification process.⁽³⁾ Recent studies by Hatcher and coworkers on the evolution of coalified woods using microscopy and NMR have led them to propose selective, acid-catalyzed, solid state reaction chemistry to account for retained structural integrity in the wood.⁽⁴⁾ However, the chemical feasibility of such reactions in relevant solids is difficult to demonstrate. We have begun a model compound study to gain a better molecular level understanding of the effects *in the solid state* of organic-mineral matter interactions relevant to both coal formation and processing. To satisfy the need for model compounds that remain nonvolatile solids at temperatures ranging to 450°C, model compounds are employed that are chemically bound to the surface of a fumed silica (Si-O-C_{aryl} linkage).⁽⁵⁻⁹⁾ The organic structures currently under investigation are phenethyl phenyl ether (C₆H₅CH₂CH₂OC₆H₅) derivatives, which serve as models for β-alkyl aryl ether units that are present in lignin and lignitic coals. The solid-state chemistry of these materials at 200-450°C in the presence of interdispersed acid catalysts such as small particle size silica-aluminas and montmorillonite clay will be reported. Our initial focus will be on defining the potential impact of these interactions on coal pyrolysis and liquefaction.

EXPERIMENTAL

The synthesis of the precursor phenol, *p*-HOPhCH₂CH₂OPh (HOPPE), has been reported.⁽¹⁰⁾ The *ortho*-methoxy derivative, *p*-HOPhCH₂CH₂OPh-*o*-OCH₃, was synthesized⁽¹¹⁾ by a similar route except the sodium salt of guaiacol, made from guaiacol and NaH in DMF, was used to alkylate the tosylate, *p*-PhCH₂OPhCH₂CH₂OTs,⁽¹⁰⁾ in toluene. The benzyl protecting group was removed by hydrogenolysis with 10% Pd on carbon in CH₃CO₂H with 0.5% H₂SO₄. The phenols were purified to >99.8% (by GC) by elution through a silica column using toluene, followed by multiple recrystallizations from benzene/hexanes.

Detailed procedures for the synthesis of silica-attached diphenylalkanes have been previously described.⁽⁵⁻⁹⁾ Briefly, the precursor phenols were covalently attached to the surface of a dried (200°C), nonporous silica (Cabosil M-5, Cabot Corp., 200 m²g⁻¹, ca. 4.5 OH nm⁻²) by a condensation reaction (225°C, 0.5 h) with the surface hydroxyl groups. For these substrates, unreacted phenol was removed by soxhlet extraction with benzene, rather than high temperature sublimation. The resulting immobilized model compounds are attached to the silica surface by a thermally robust Si-O-C_{aryl} linkage. Surface coverages (ca. 0.25 mmol g⁻¹) were determined by GC analysis using internal standards following a standard base hydrolysis assay.⁽⁵⁻⁹⁾

The silica-immobilized substrates were blended 1:1 with a dried, fumed silica-1% alumina (Aerosil MOX 170, Degussa, 170 m²g⁻¹; 15 nm average particle size), silica-15% alumina (Aerosil COK 84, Degussa, 170 m²g⁻¹), or montmorillonite clay (Montmorillonite K-10, Aldrich, 220-270 m²g⁻¹, <1μ particle size).^(9,11) Similar results were obtained when the solids were either dry mixed or when they were dispersed in benzene followed by solvent evaporation. Thermolyses were performed at 200-450°C (±1.5°C) in sealed tubes under vacuum in a temperature controlled, fluidized sandbath, or in a temperature controlled tube furnace as

previously described.⁽⁵⁻⁹⁾ Volatile products were trapped in liquid nitrogen, and analyzed by GC and GC-MS with the use of internal calibration standards. Surface-attached products were liberated as phenols following digestion of the silica with aqueous base, silylated to the corresponding trimethylsilyl ethers, and analyzed as above.

RESULTS AND DISCUSSION

The two model compounds examined thus far are silica-immobilized phenethyl phenyl ether ($\approx\text{PhCH}_2\text{CH}_2\text{OPh}$, or $\approx\text{PPE}$) and the corresponding methoxy derivative ($\approx\text{PhCH}_2\text{CH}_2\text{OPh}-o\text{-OCH}_3$, or $\approx\text{PPE}-o\text{-OMe}$) as shown in Figure 1. These compounds are models for the β -aryl ether linkages present in lignin and low rank coals. $\approx\text{PPE}-o\text{-OMe}$ contains the guaiacyl unit that is abundant in gymnospermous lignin.⁽¹²⁾

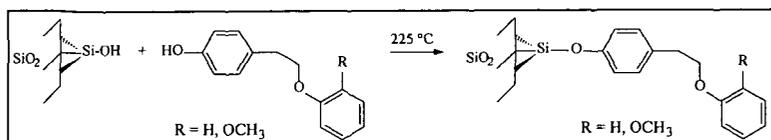


Figure 1. Preparation of silica-attached phenethyl phenyl ether derivatives.

A comparison of the principal products from the thermal and SiO_2 -1% Al_2O_3 -catalyzed reactions for $\approx\text{PPE}$ at 400°C is shown in Figure 2. In the absence of the silica-alumina, the products are readily explained by a free-radical chain decomposition pathway.⁽¹¹⁾ In the presence of the small particle size silica-alumina, the rate of reaction for $\approx\text{PPE}$ is increased by a factor of three (from 69 to $216\% \text{ h}^{-1}$), and the product distribution is substantially altered. At 400°C where the free-radical and acid-catalyzed reactions can compete, the product distribution is dominated by acid-catalyzed cracking products. A similar product distribution is obtained when the silica-alumina catalyzed reaction is performed at the lower temperature of 300°C , where the free-radical reaction is suppressed.

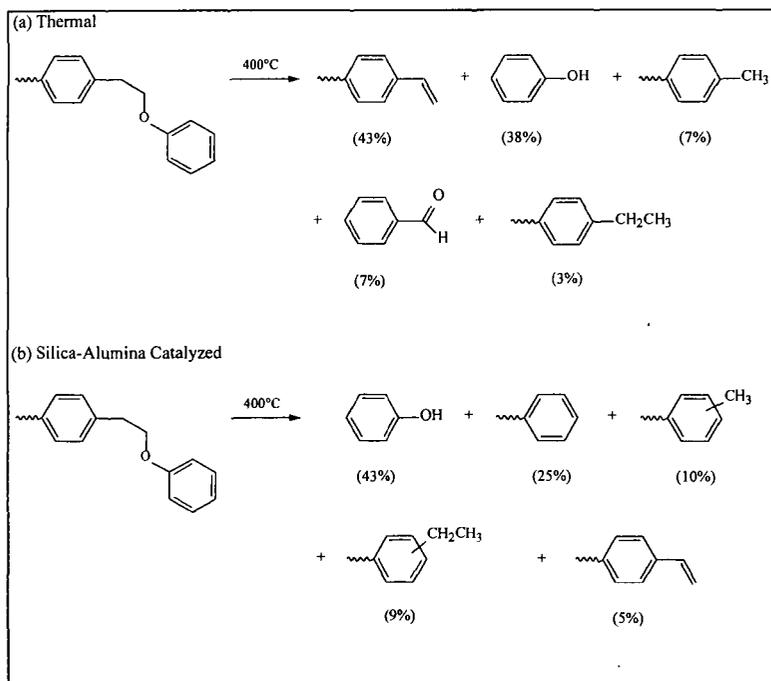


Figure 2. Solid-state reaction for $\approx\text{PPE}$ at 400°C for 15 min in the (a) absence and (b) presence of a silica-alumina catalyst.

The acid-catalyzed products arise from two reaction pathways involving (1) initial protonation of the ether oxygen followed by cracking of the ether linkage to form phenol and silica-attached phenethyl cation ($\approx\text{PhCH}_2\text{CH}_2^+$), or (2) protonation of the surface-attached phenyl ring followed by cleavage to produce $\approx\text{PhH}$ (*ipso*-protonation) or $\approx\text{PhCH}_3$ (*ortho*- or *para*-protonation).⁽¹¹⁾ The silica-attached alkyl benzene products are found to be isomerized to *ortho*-, *meta*-, and *para*-isomers. Furthermore, we observe that alkenes are not stable under these conditions and represent minor products in the presence of the silica-alumina. The mass balances, which are excellent in the non-catalyzed runs (ca. 99%), are substantially diminished in the presence of silica-alumina. The mass balances are 79% at 400°C and 54% at 450°C principally as a consequence of coking reactions on the silica-alumina.

Similar behavior is observed for $\approx\text{PPE-}o\text{-OMe}$ whose thermally induced, free-radical reaction (Figure 3) parallels that for $\approx\text{PPE}$, but whose rate is ca. seven times faster as a consequence of the *ortho*-methoxy substituent.⁽¹¹⁾ Again in the presence of the silica-alumina, acid-catalyzed reactions dominate and are analogous to those observed for $\approx\text{PPE}$. Protonation of the β -aryl ether, followed by cleavage produces guaiacol (*o*-methoxyphenol) as the major product at 300°C (46%). However, at 400°C (Figure 3) as a result of the higher reactivity of $\approx\text{PPE-}o\text{-OMe}$, conversions in excess of 85% are obtained in only 10 min. The dominant products at 400°C are the alkylated benzenes, $\approx\text{PhH}$, $\approx\text{PhCH}_3$, and $\approx\text{PhCH}_2\text{CH}_3$ with guaiacol accounting for only 13% of the products.⁽¹¹⁾ Isomerized (**1**) and alkylated (**2**) starting material are also detected. Coking of the aluminosilicate is again significant and mass balances are low (ca. 40%). Small amounts (2-5%) of catechol (*o*- $\text{Ph}(\text{OH})_2$) are obtained at 275-400°C indicating that demethylation at the methoxy substituent is a minor reaction pathway under these conditions.

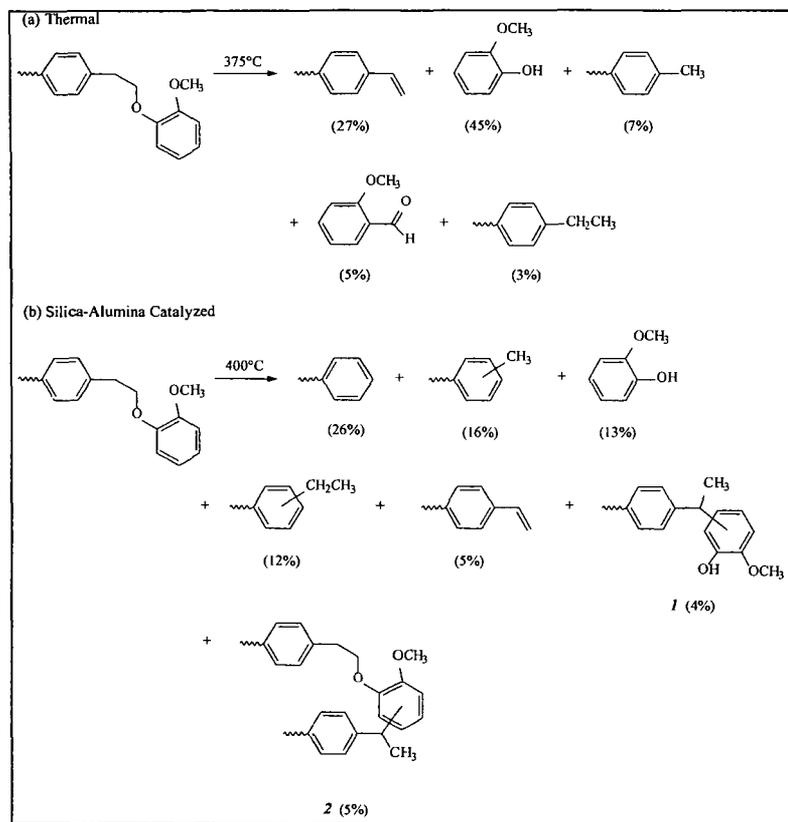


Figure 3. Solid-state reaction for $\approx\text{PPE-}o\text{-OMe}$ in the (a) absence and (b) presence of a silica-alumina catalyst.

SUMMARY

The solid-state chemistry of silica-immobilized phenethyl phenyl ethers is being investigated in the presence of interdispersed silica-aluminas at temperatures (300-450°C) relevant to coal processing to gain a better understanding of the impact of related mineral matter on coal pyrolysis and liquefaction mechanisms. The results demonstrate the dramatic effect that silica-aluminas can have in altering the normal thermal reaction pathways for these models of ether linkages in lignin and low rank coals. At temperatures where free-radical reactions and acid-catalyzed reactions can compete, the products are dominated by acid-catalyzed cracking reaction pathways. The yields of alkenes are dramatically reduced, while new products from aromatic dealkylation, rearrangement, and alkylation are observed. Although the presence of silica-alumina assists in the cracking of the ether models, they also lead to the formation of nonvolatile, higher aromatic residues, i.e. coke. An investigation of the chemistry of these model compounds at low temperatures (ca. 150-200°C) in the presence of silica-aluminas, including montmorillonite, is also in progress to delineate the chemical transformations that can occur during lignin maturation.

ACKNOWLEDGEMENTS

This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. The authors also thank Ms. Kimberly Thomas for technical assistance.

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