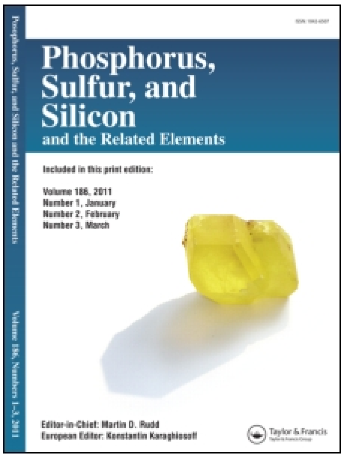

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PREPARATION OF ORTHO-(ALKYLTHIO)PHENOLS OVER ZEOLITE CATALYSTS

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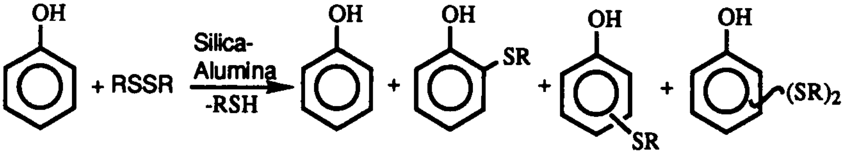
Abstract Amorphous and crystalline (zeolite) aluminosilicates are good catalysts for the alkylthiolation of phenols with disulfides. Zeolites offer product selectivity via catalyst shape selectivity. Product distribution equilibrations are operative, and distributions depend upon reaction time, temperature, catalyst, and stoichiometry. Aluminosilicate and Bronsted acid catalysts give para-(alkylthio)phenols as the major kinetic product while metal phenoxides give ortho as the major. All catalysts give ortho as the major thermodynamic product.

INTRODUCTION

Ortho-(alkylthio)phenols are useful intermediates for the preparation of agricultural chemicals and pharmaceuticals. Their preparation has been reported by alkylthiolation of phenols with dialkyl disulfides using acid catalysts. Bronsted acids such as sulfuric, phosphoric, PPA, ion-exchange resins, sulfonic acids[1], and clays[2] reportedly give para-(alkylthio)phenols as the major product, while acid catalysts containing the metals iron[2], aluminum[2,3], and zirconium[4] reportedly give ortho as major. The use of aluminosilicates as catalysts is reported here.

ALKYLTHIOLATION OF PHENOLS

A typical aluminosilicate reaction is shown below.



(1)

2 hr	104°C	90	3	5 (m+p)*	2%
4	120	65	16	16	3
24	120	47	32	12	10

* Little or no meta under these conditions.[5]

Typical reaction conditions used were no or excess phenol as solvent, equimolar or greater phenol than disulfide, catalyst/disulfide 0.2-0.6 weight ratio, temperatures of 100-130°C, and reaction times of 2-24 hours. Atmospheric pressure was used and mercaptan by-product allowed to escape continuously. Product distributions changed with time as shown above. Reaction in the vapor phase at 270-400°C gave desulfurization.[5]

Aluminosilicate catalysts studied were amorphous (silica-alumina) and crystalline (zeolitic). Over 20 zeolites differing primarily in structure were studied.

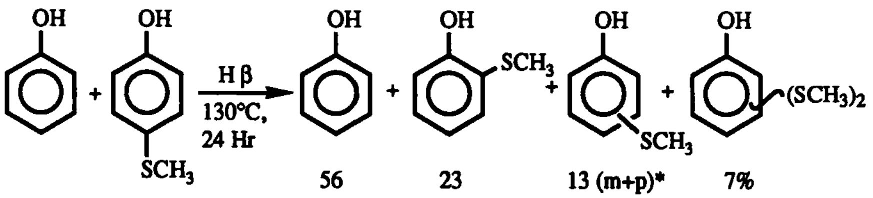
Reaction rates in general were found to be directly proportional to catalyst acidity.[6] No reaction was observed with the weak acids gamma-alumina or silica-gel. Zeolites displayed shape selectivity which manifested itself in product reaction type, shown in the table below, and reaction rate. Thus, for example, large pore H Y gave faster reaction than medium pore H ZSM-5 although the latter is much more acidic.

Zeolite Pore Size		Example	Alkylthiolated Product
Small	3-4 Å	H Erionite	No Reaction
Medium	5-6 Å	H ZSM-5	Mono Substituted Only
Large	7 Å	H Y, H β	Mono, Di and Higher Sub.
Amorphous		SiO_2-Al_2O_3	Mono, Di and Higher Sub.

Only internal zeolite catalyst sites were used. This was shown by no reaction with small pore zeolites, and by observing that medium and large pore zeolites whose external sites were coated with inert alumina[7] gave identical products and rates as uncoated catalyst. Aluminosilicates were found to be reusable repeatedly, and if fouled, rejuvenated by burning in air, e.g., at 500°C for 16 hours.

ALKYLTHIO GROUP EQUILIBRATION

Aluminosilicates were found to equilibrate alkylthio groups on phenols.[8] A typical reaction is shown below.



(2)

* Little or no meta under these conditions.[5]

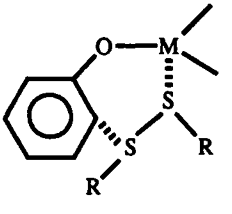
The formation of ortho isomer indicates equilibration. Disubstituted product indicates that the mechanism is bimolecular (intermolecular).[9] Whether equilibration proceeds by two molecules joining to form one intermediate, the deposition of an alkylthio group on the catalyst by one molecule followed by its removal by another, both, or otherwise is uncertain. The absence of meta isomer suggests the mechanism is not unimolecular (intramolecular), i.e., proceeding by 1,2-shifts. Equilibration occurs under the same reaction conditions as thiolation with disulfide and likely accounts for product distribution changes with time in Equation 1.

Equilibrations over zeolites (Equation 2) display catalyst shape selectivity. Thus large pore H Y rapidly gives mono, di, and higher substituted products while medium pore H ZSM-5 slowly gives only mono despite its greater acidity.

More severe reaction conditions, e.g., 150-180°C for 30-100 hours using strong acids, have produced ortho, meta, para mixtures containing up to 33% meta. Ortho consistently remained the favored isomer with ortho:para observed as high as 4:1.[5] Ortho is favored presumably due to H-bonding.

ALUMINOSILICATES AND BRONSTED ACIDS VERSUS METAL PHENOXIDE CATALYSTS

Product distribution changes during alkylthiolation of phenols with disulfides revealed that aluminosilicates and Bronsted acids initially gave para isomer as the major product, i.e., in kinetically controlled mixtures. Ortho became major only after continued heating, i.e., with equilibration to thermodynamically controlled mixtures (Equation 1). In contrast, metal (Al, Zr) phenoxide catalysts under similar reaction conditions gave ortho as the major product throughout. Metal phenoxides presumably ortho-direct by electronic activation of the ortho position[10] as well as an orientation affect, i.e. formation of a 6-membered ring complex.



REACTION SCOPE

The chemistry in Equation 1 has also been used to introduce alkylthio groups in good yield into the ortho position of phenols containing para-methyl or para-chloro substituents. There is no evidence of methyl migration. Successful disulfides in Equation 1 include methyl, ethyl, n-propyl, n-butyl, and phenyl. t-Butyl and benzyl disulfides gave ring alkylated, but not thiolated phenols. When thiophenol was used in place of phenol, reaction did not occur on the ring, but on sulfur to yield phenyl alkyl disulfides.

Additional examples of this chemistry with experimental details are given in P. W. Wojtkowski, U.S.P. 4,792,633, 2/20/88, assigned to E. I. du Pont de Nemours and Company.

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