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## Electrophilic Alkenylation of Aromatics with Phenylacetylene over Zeolite HSZ-360

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*Abstract:* Aromatic compounds react with phenylacetylene in the presence of zeolite HSZ-360 affording 1,1-diarylethylenes 3 in good to excellent yields and selectivities.

A vast amount of work has been and is being devoted to the development and the use of heterogeneous catalysts for petrochemical processes as well as synthesis of intermediates and fine chemicals.<sup>1</sup> Most of this interest comes from the fact that heterogeneous catalysis gives a new dimension to the synthetic organic chemistry in terms of yield, selectivity, work-up and effluent pollution.<sup>2</sup>

In a series of early studies concerning the metal-template catalysis on phenol substrates we have reported the synthesis of *ortho*-alkenylphenols by reaction of bromomagnesium and aluminium phenolates with phenylacetylene,<sup>3</sup> ketals<sup>4</sup> and ketones.<sup>5</sup> More recently a direct alkenylation of phenols with 1-alkynes promoted by tin tetrachloride and tributylamine was described.<sup>6</sup>

Table 1. Reaction of phenol with phenylacetylene in the presence of heterogeneous catalyst."



Catalyst		Yield (%)	Selectivity (%) <sup>§</sup>	
HSZ-360 - Y Zeolite	(Tosoh Corp.)	38	94	
ZSM-5 - Y Zeolite	(BDH)	10	55 _	
K10 - Montmorillonite	(Fluka)	5	35	
KSF - Montmorillonite	(Fluka)	24	60	

Reaction conditions: phenol (10 mmol), phenylacetylene (10 mmol), catalyst (1 g).

\* Products of para-alkenylation and polyalkenylation were also detected.

<sup>1</sup> Selectivity = Yield/Reacted phenol x 100.

As part of a program aimed at achieving new, simple and environmentally compatible synthetic methodologies, we have re-examined the electrophilic alkenylation of aromatic substrates with phenylacetylene in the presence of an heterogeneous catalyst. Here we report some results of this study.

The catalyst utilised was the Y-type zeolite HSZ-360 supplied by Tosoh Corporation since in preliminary experiments this catalyst was found to be the best promoter of the *ortho*-regioselective alkenylation of phenol with phenylacetylene to give 1-(2-hydroxyphenyl)-1-phenylethylene in comparison with other commercially available catalysts as reported in Table 1.

The X-ray powder diffraction pattern of the catalyst HSZ-360 is shown in Fig.1 (a)<sup>7</sup> and matches well the tabulated diffraction pattern for faujasite shown in Fig.1 (b) for comparison.<sup>8</sup>

Before use the catalyst (H-form) was heated at 120°C for 10 hours under dry nitrogen. All reactions were carried out as follows: 1.0 g of the catalyst was added to a solution of phenylacetylene (1.0 g; 10 mmol) and the selected aromatic compound (10 mmol) in dry *ortho*-dichlorobenzene or decaline (6 ml). The mixture was heated at 110°C under stirring for 14 hours. After cooling to room temperature, filtration and distillation of the solvent, products were purified by flash chromatography (eluant hexane/ethyl acetate: 90/10). Benzene, xilenes and mesitylene were utilized as solvent reagents.



Fig 1. The X-ray powder diffraction pattern of HSZ-360 (a) and the tabulated pattern of faujasite (b).

As clearly emerges from synthetic results reported in the Table 2, yields and selectivities of products 3 are satisfactory or excellent and are consistent with a typical electrophilic substitution process. Competitive isomerization and transalkylation were never observed in the reaction with xilenes and mesitylene (entries b, c and d); moreover, only products of monoalkenylation were detected in all cases. Concerning the absolute orthoregioselective control observed with the phenol (entry f), the product 3f is likely formed through the intervention of an hydrogen bond between the hydroxy group and the alkyne on the analogy of the ortho-regioselective alkylation of phenols with alkenes promoted by aluminium phenolates.<sup>9</sup> In fact, when anisole was reacted under the above conditions, a 1:1 mixture of ortho- and para-phenylethenylanisoles was obtained.

As regards the phenylacetylene, variable amounts of acetophenone (5-20%) were detected in all experiments due to the competitive reaction with traces of water linked to the catalyst.<sup>10</sup> On the other hand, attempted use of a completely dried catalyst resulted in a remarkable lowering of reactivity. Compound **3f** was obtained in 10-12% yield by using HSZ-360 previously heated at 500°C for 10 hours or heated under high vacuum at 280°C for 10 hours or dried by azeotropic distillation in toluene for 60 hours.

Concerning the interaction with the catalyst both reactants could diffuse through the pores of HSZ-360 which dimension is 8 Å<sup>11</sup> but, in our opinion, the reaction in the pores is prevented because the transition state for the *ortho*-alkenylation involves both the aromatic substrate and phenylacetylene and is too bulky for the cavities of the catalyst.<sup>12</sup> Thus, from these preliminary data, it seems likely that the reaction occurs on the external surface of the catalyst particles. In fact, by reacting 1f with 2 in the presence of acid alumina<sup>13</sup> under the same

Table 2. Reaction of aromatics with phenylacetylene<sup>14</sup> over zeolite HSZ-360.

	ArH → PhC≡0	HSZ-360			
	1 2	1,2-dichloro	obenzene, 110°C, 14 h	Ar Ph	
Entry	Substrate 1	Conversion (%)	Product 3	Yield (%)	Selectivity (%)
a	$\bigcirc$	49ª	C Ph	40	82
b	¢	91ª	Ph Ph	80	88
c		94 <sup>ª</sup>	Ph Ph	80	85
d	ţ,	99ª	,↓↓↓Pħ	94	95
e	$(\mathfrak{X})$	80 <sup>b</sup>	CCC Ph	70°	88
f	OH C	55 <sup>6</sup>	Ph	52	95
g	OH	94 <sup>ь</sup>	OH Ph	90	96
h	OH COH, COH,	70 <sup>6</sup>		65	93
i	())) <sup>OH</sup>	93 <sup>b</sup>	Ph OH	90	97
j	0H	74 <sup>b</sup>	Ph	70	95

Conversion calculated with respect to the phenylacetylene.
<sup>b</sup> Conversion calculated with respect to the aromatic substrate.
<sup>c</sup> 8% yield of α-attack was also detected.

conditions, the product 3f was obtained in lower yield (25%), but with the same high *ortho*-regioselectivity (96%).

In summary, we report our preliminary results on the use of zeolite HSZ-360 as an efficient catalyst for alkenylation of aromatics with phenylacetylene. This study is currently under progress.

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- 10. Acetophenone was found to be totally ineffective in the present reaction being recovered unchanged after treatment with phenol, under the described reaction conditions.
- 11. Information kindly furnished by Tosho Corporation.
- 12. The kinetic diameter of benzene based on the Lennard-Jones relationship is 5.85 Å: Csicsery, S.M. Zeolites, 1984, 4, 202.
- 13. Acidic alumina (Carlo Erba) for chromatography was utilized.
- 14. 1-octine and 1-hexine underwent migration of carbon-carbon triple bond along the chain leading to a complex mixtures of isomeric alkynes accompanied by traces of alkenylphenols.

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