

A HIGHLY SELECTIVE METHOD FOR THE SYNTHESIS OF PHENYLACETALDEHYDE

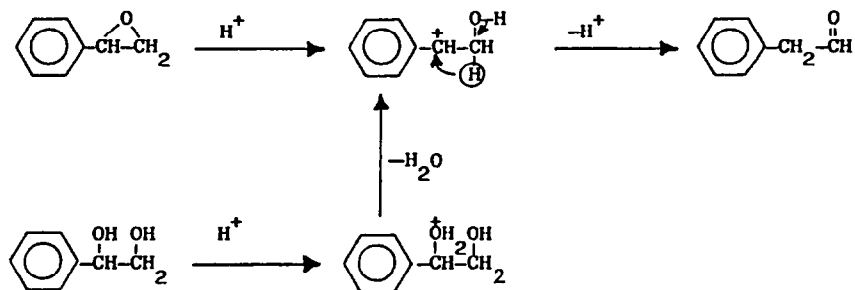
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Abstract: Phenylacetaldehyde is synthesized in high yield by isomerization of styrene oxide and by dehydration of styrene glycol in gas phase using H-ZSM-5 zeolite, Silicalite and silica gels as catalysts.

Phenylacetaldehyde is used in manufacturing of perfumery products and could become a useful intermediate in many organic syntheses of industrial interest. A very relevant use could be for phenylalanine synthesis (1). However its use as intermediate has been limited because there was not an easy and economical method to synthesize it. Phenylacetaldehyde can be prepared by various methods: from benzaldehyde by the Darzens Glycidic Ester Condensation (2) and by isomerization of styrene oxide both in liquid (3) or in gas phase (4). According to the reported methods the yields of phenylacetaldehyde were not very high. The dehydration of styrene glycol was also reported with poor results (5). The aim of this paper is to show the use of zeolites and other silica based catalysts to convert styrene oxide and styrene glycol to phenylacetaldehyde in almost quantitative yield (see Table). The reactions are carried out in a fixed bed catalytic reactor fed by a gaseous mixture of reagent and steam. Four classes of catalysts were tested: zeolitic materials (H-ZSM-5 and Silicalite), amorphous silica gels, alumina and silica-alumina. The zeolitic catalysts H-ZSM-5 and Silicalite were synthesized according to patent literature (6). Silicalite is a crystalline material structurally similar to H-ZSM-5 zeolite, without any alumina in the framework. The silica gels, alumina and silica-alumina were commercial catalysts. A test for the different Silica's acidity is the pH of an aqueous slurry at 10% w/w of the sample. Both the styrene oxide rearrangement and glycol dehydration are acid catalyzed reactions where the benzylic cation is probably the common intermediate.



The strength of the acid sites is important for the productivity of the catalysts (see Table) but does not influence their selectivity. The best results were obtained with the crystalline catalysts: H-ZSM-5 zeolite and Silicalite. Also some silica gels give good yields but with lower space velocity. With the catalysts having both acidic and basic sites such as silica-alumina and alumina there is the formation of byproducts and deactivation of the catalyst. This probably results from the phenylacetaldehyde disproportionation with formation of phenylacetic acid and other heavy byproducts. Considering the molecular size of the reactants and of the products we can conclude that the reaction on zeolite H-ZSM-5 and on Silicalite should occur on the acidic sites of the external surface of the crystals. There are other examples where these sites play an important role in catalysis (7).

TABLE: Vapour phase preparation of phenylacetaldehyde in a continuous flow reactor

RUN	SUBSTRATE	CATALYST	T °C	TIME OF STREAM h	WHSV(*)	YIELD (*)	CONVERSION (*)
					h ⁻¹		
1	Styr. Oxide	H-ZSM-5	200	6	30	96	99
2	Styr. Oxide	Silicalite	250	4	20	96	99
3	Styr. Glycol	H-ZSM-5	200	6	30	97	99
4	Styr. Glycol	H-ZSM-5	250	6	30	98	100
5	Styr. Glycol	Silicalite	250	4	15	97	99
6	Styr. Glycol	Silica Gel (A)	250	6	5.5	96	99
7	Styr. Glycol	Silica Gel	270	6	5	96	100
8	Styr. Glycol	Silica Gel	300	6	10	96	99
9	Styr. Glycol	Silica Gel	325	6	15	95	98
10	Styr. Glycol	Silica Gel (B)	250	1	5	60	63
11	Styr. Glycol	Silica Gel (C)	200	1	5	3	3
12	Styr. Glycol	Silica Alumina	250	4	5	60	65
13	Styr. Glycol	γ-Alumina	250	2	5	15	20

The organic substrate was vaporized and diluted with steam (3:1 w/w).

WHSV (g/h/g) is referred to the organic substrate.

A, B, and C were silica gels giving pH 4.3, 5.5, 6.4 respectively in 10% w/w aq. slurry.

(*) Calculated on G.C. basis.

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