Catalytic use of zeolites in the Prins reaction of arylalkenes

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The Prins reaction of various arylalkenes with paraformaldehyde on different zeolites as solid acid catalysts was studied. The main product of the reaction under the experimental conditions used was found to be the corresponding 1,3-dioxane. Of the catalysts tested, beta (75) zeolite proved the most active and selective in the Prins reaction of styrene, with a selectivity of 41.4% and a conversion of 95%. Other zeolites such as USY and, especially, ZSM-5, provided much lower yields. The reactions of other arylalkenes were found to be strongly influenced by the substituents on the double bond.

KEY WORDS: Prins reaction; arylalkenes; paraformaldehyde; 1,3-dioxanes; zeolites

1. Introduction

Substantial effort has lately been expended on the development of increasingly clean chemical procedures and, especially, on the production of fine chemicals [1]. Heterogeneous catalysts provide a number of advantages of environmental interest including easy isolation and recovery from the reaction medium. In addition, a number of available catalytic solids exist that span a broad range of acid–base and redox properties. Many organic processes are catalysed by acid [2] or basic solids [3]. Among acid catalysts, zeolites have probably received the greatest attention of all, as a result of their combined acid–base and shape-selectivity properties [1,4]. Thus, zeolites have been used as catalysts in Friedel–Crafts and addition reactions, which are especially interesting for the production of fine chemicals. The former include aromatic acylation [5] and the alkylation of naphthalene with propene, which yields 2,6-diisopropylnaphthalene with quite good selectivity on mordenite thanks to the shape-selectivity of the catalyst's pore network [6]. The addition reactions include the Koch synthesis leading to pivalic acid [7].

The so-called "Prins reaction" involves the addition of carbonyl compounds to alkenes to obtain a complex mixture of products. The process is catalysed by mineral Brønsted acids (e.g., H_2SO_4, H_3PO_4, CH_3COOH) and by some Lewis acids (e.g., BF_3, $SnCl_4$). The carbonyl compound involved is usually formaldehyde [8–10]. This reaction is especially interesting with a view to the formation of carbon–carbon bonds; its use in organic synthesis has so far been restricted by the operating conditions required and the fact that it often yields a complex mixture of products.

The Prins reaction between acetaldehyde and ethylene has been used to account for the formation of a small amount of butadiene in the conversion of ethanol on silver-exchanged aluminated sepiolite [11]. That between isobutylene and formaldehyde in the gas phase over various molecular sieves, which yields isoprene, has been extensively studied and its selectivity found to be influenced by pore size and acid strength [12–16].

The synthesis of 3-methyl-3-butene-1-ol (MBOH) from isobutylene and formaldehyde in the liquid phase has been carried out over various zeolites. The optimum conditions were obtained over FeMCM-22, which is about 90% selective for MBOH with 45% formaldehyde conversion [17].

In this work, the potential of various zeolites as catalysts for the Prins reaction of styrene and paraformaldehyde in the liquid phase was assessed. Various other arylalkenes were also tested as reactants.

2. Experimental

The catalysts used were various zeolites purchased from Zeolyst International and an acidic Al_2O_3 from Aldrich. The number in brackets following their names indicates the Si/Al ratio. All solids were previously activated by heating at 500 °C for 3 h.

Acid sites were quantified from the retention isotherm for pyridine ($pK_a = 5.25$) dissolved in cyclohexane. The amount of titrant retained by each solid was measured spectrophotometrically ($\lambda = 250$ nm). By using the Langmuir equation, the amount of titrant adsorbed in monolayer form, X_m, was obtained as a measure of the concentration of acid sites [18,19].

All reactions were conducted in a flask that was fitted with a reflux condenser and filled with a mixture of 8.6 mmol of the arylalkene concerned, 1.0 g of paraformaldehyde and 5 ml of solvent. Following addition of the catalyst (usually 0.200 g), the mixture was refluxed under magnetic stirring. The catalyst was then filtered off and washed to obtain the final mixture of products.

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Table 1
Results obtained in the Prins reaction of styrene with paraformaldehyde on various zeolites.[a]

Catalyst(Si/Al)	Acidity (10^{-4} mol g^{-1})	Conversion (mol%)	Yield (mol%)		Selectivity (%)	
			4-phenyl-1,3-dioxane	Cinnamyl alcohol	4-phenyl-1,3-dioxane	Cinnamyl alcohol
Acid Al_2O_3	0.9	50.4	–	–	–	–
ZSM-5(40)	4.3	65.7	7.9	–	12.1	–
USY(30)	5.6	61.8	18.6	–	30.2	–
Ferrierite(27.5)	1.2	70.0	25.8	–	36.8	–
Beta(12.5)	7.3	77.5	28.3	2.9	36.5	3.8
Beta(37.5)	6.0	87.8	33.5	–	38.2	–
Beta(75)	5.3	95.0	39.3	5.9	41.4	6.2
Mordenite(10)	6.5	48.2	18.2	–	37.7	–
Mordenite(45)	3.6	59.8	23.0	–	38.4	–

[a] See text for reaction conditions. Solvent 1,4-dioxane, amount of catalyst 0.200 g, reaction time 15 h.

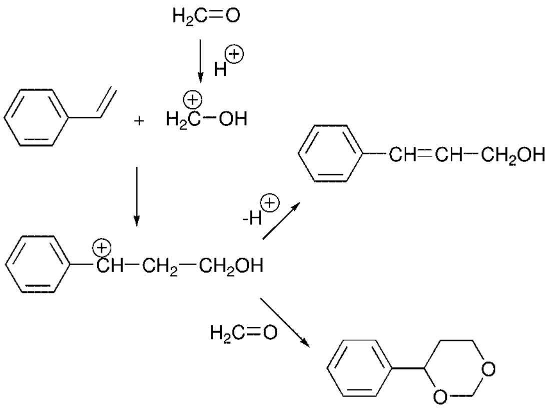
Samples were analysed by gas chromatography, using an HP-1 12 m × 0.2 mm ID methyl silicone capillary column and raising the temperature from 100 to 200 °C at 10 °C min^{-1}. Reaction products were identified by use of standards and mass spectrometry, and quantified with cumene as internal standard.

3. Results and discussion

Table 1 shows the results obtained in the Prins reaction of styrene on various zeolitic catalysts under the studied reaction conditions. The formaldehyde source used was paraformaldehyde. The only reaction products detected were cinnamyl alcohol and 4-phenyl-1,3-dioxane (scheme 1). The reaction involves the protonation of the C=O bond in formaldehyde at an acid site of the catalyst, which produces a carbocation that attacks the alkene's double bond. The intermediate carbocation can evolve by releasing a proton to give cinnamyl alcohol or by reacting with formaldehyde again to form the corresponding dioxane. The main reaction product obtained with all the zeolites studied was the corresponding 1,3-dioxane.

The highest conversion and selectivity were obtained with beta zeolite, which has proved an excellent catalyst for acid-catalysed organic processes of interest to fine chemistry [1,20,21]. No reaction products were detected in the process conducted on an acid Al_2O_3 solid, even though the styrene conversion was in the region of 50%. Of all the zeolites tested, ZSM-5 was that providing the lowest yield in the reaction products and hence the lowest selectivity. This suggests that the reaction does not require the high acidity of this zeolite and that the small pore size of this solid is probably the greatest hindrance for the reaction to develop. On the other hand, beta zeolite, which possesses a fairly high acidity and large pores forming an interesting three-dimensional network of elliptical channels, provided the highest dioxane yield.

Our results show that beta zeolite is a more effective catalyst for the conversion of styrene into 1,3-dioxanes via the Prins reaction than are sulphuric, *p*-toluenesulphonic and heteropoly acids (especially $H_4GeW_{12}O_{40}$, which exhibits a styrene conversion of 25.5%) [22]. However, the results are not as good as those provided by some cation-exchanged montmorillonites, particularly those containing Ce^{3+} and Fe^{3+} [23], which provided isolated yields up to 99%.



Scheme 1.

The effect of the solid acidity on the reaction was examined by using various beta zeolites and mordenites with different Si/Al ratios. Table 1 summarizes the acid site concentration of the catalysts studied. As expected, with a given zeolite, the concentration of Brønsted acid sites decreased with decreasing Al content. Our results suggest that the zeolite acidity has negligible influence on the reaction; on the other hand, an increased Si/Al ratio (i.e., lower acidity) results in slightly higher total conversion and dioxane yield. The Si/Al ratio also determines the strength of acid sites. However, in the case of beta zeolite with Si/Al $>$ 8 all Al will be isolated and all the corresponding bridging hydroxyl groups should be equivalent, with the maximum acid strength obtainable for a particular structure [24]. The Prins reaction of isobutylene with formaldehyde was found to exhibit a high selectivity for isoprene only when the catalyst used possessed Brønsted acid sites of low-to-medium strength (viz. those needed to selectively protonate formaldehyde but not the olefin to a carbocation [14]). The Si/Al ratio also affects the adsorption properties of the zeolite, particularly its hydrophobicity–hydrophilicity. This variable should be important because the Prins reaction involves a highly hydrophobic reactant (styrene), which has to diffuse through the pores and adsorb in the zeolite. Accordingly, those zeolites with an increased Si/Al ratio (i.e., increased hydropho-

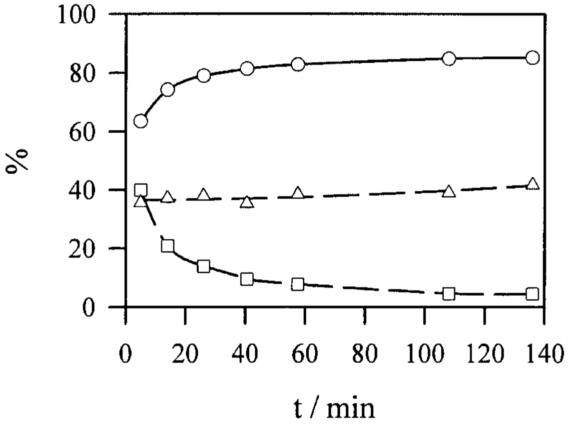


Figure 1. Overall conversion (mol%) (○), and selectivity towards cinnamyl alcohol (□) and 4-phenyl-1,3-dioxane (△), in the Prins reaction of styrene with paraformaldehyde on beta(37.5) zeolite. For reaction conditions see table 1.

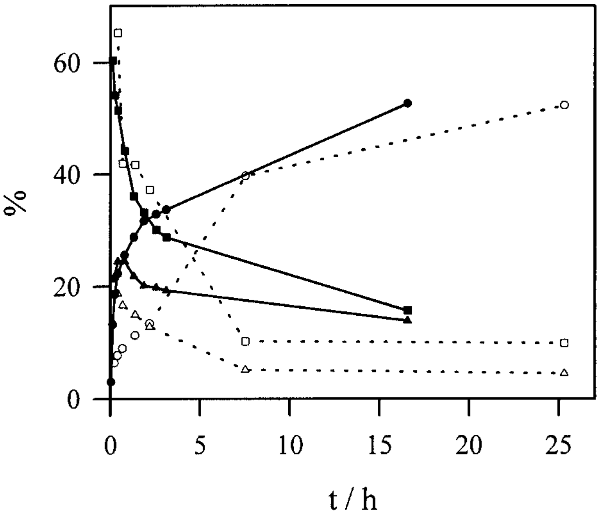


Figure 2. Influence of the amount of catalyst on the overall conversion (mol%) (○), and the selectivity towards cinnamyl alcohol (□) and 4-phenyl-1,3-dioxane (△), in the Prins reaction of styrene with paraformaldehyde on beta(75) zeolite: 0.025 (- - -), 0.100 g (—). For reaction conditions see table 1.

Table 2
Overall conversion, and yield and selectivity towards 4-phenyl-1,3-dioxane, in the Prins reaction of styrene with paraformaldehyde on beta(75) zeolite in different solvents.[a]

Solvent	Conversion (mol%)	Yield (mol%)	Selectivity (%)
Chloroform	41.8	18.2	43.6
Benzene	25.4	13.2	52.0

[a] For reaction conditions see table 1.

Table 3
Overall conversion, and yield and selectivity towards 1,3-dioxanes, in the Prins reaction of substituted styrenes and cyclohexene with paraformaldehyde on beta(75) zeolite.[a]

Alkene	Conversion (mol%)	Yield (mol%)	Selectivity (%)
α-methylstyrene	100	32.4	32.4
trans-β-methylstyrene	66.0	50.3	76.2
trans-β-nitrostyrene	<4	–	–
Cyclohexene	73.6	17.8	24.2

[a] For reaction conditions see table 1.

bicity) are slightly better for the intended purpose than are more hydrophilic zeolites (table 1), due to their improved adsorption properties for non-polar molecules. Increased hydrophobicity has been found to favour other processes such as acylation [25], hydration [26] and glucosidation [24,27].

Figure 1 shows the temporal evolution of a selected Prins reaction. As can be seen, the 4-phenyl-1,3-dioxane yield increased with time (from 22.7% at 5 min to 35.7% at 136 min); on the other hand, the cinnamyl alcohol yield decreased from 25.4 to 3.8% over the same length of time. This suggests that the alcohol is used in side reactions that yield other compounds which could not be detected by GC. In addition, the total conversion was very high from the start. Figure 2 illustrates two more experiments conducted with different amounts of catalyst. Note that long-term conversion was very similar (in excess of 50%) in both cases, even though the yields in both compounds increased with increasing amount of catalyst. These results, together with those in table 1, suggest that styrene takes part not only in the Prins reaction but also in other, side processes that result in appreciable total conversion values even though no specific reaction product is detected (see entry 1 in table 1). This was confirmed by the fact that a reaction conducted under identical conditions using beta(75) zeolite but no paraformaldehyde provided a styrene conversion of 53%. The reaction between isobutylene and formaldehyde [12–15] involves various side processes including oligomerization, polymerization, aromatization and cracking of the olefins present, all of which decrease the selectivity towards isoprene. Some olefins are known to form oligomers by interaction with strong Brønsted sites [28]; reactions of this type are probably involved in our processes as the product of the Prins reaction was normally the only one detected by GC. The formation of oligomers would gradually poison the catalyst by blocking its pore network.

As can be seen from table 2, alternative solvents such as $CHCl_3$ and benzene provided poorer results than 1,4-dioxane. Also, water present in the reaction medium, and residual water in those solids that were not previously activated by heating, was found to completely inhibit the Prins reaction, probably through adsorption at the most active sites in the catalysts. The use of an aqueous solution of formaldehyde instead or paraformaldehyde thus resulted in no reaction, unlike previously reported processes in the gas phase [15].

Beta(75) zeolite was also tested as catalyst for the Prins reaction of other arylalkenes (table 3). While the reaction of *trans*-β-methylstyrene exhibited good selectivity towards 5-methyl-4-phenyl-1,3-dioxane, that of α-methylstyrene, which was quantitative, provided a mixture of various compounds and hence decreased selectivity for the 1,3-dioxane. On the other hand, the presence of an electron-withdrawing substituent in the arylalkene (e.g., in β-nitrostyrene) destabilized the carbocationic reaction intermediates and resulted in a very low conversion (4%). Finally, the reaction of cyclohexene exhibited a low selectivity towards the corresponding dioxane, which, however, was the major product as revealed by GC.

4. Conclusions

The results of this work demonstrate that some zeolites are effective catalysts for the Prins reaction of arylalkenes. Specifically, beta zeolite provided the highest yield in the corresponding 1,3-dioxane – even higher than those obtained with previously used catalysts and with substantial advantages of environmental and industrial interest. This compound could be used as an intermediate to obtain 1,3-glycols by acid hydrolysis or 3-arylpropanol by catalytic reduction. Some cyclic acetals even undergo rearrangement to aldehydes in the presence of pentasil zeolites at a high temperature [29]. Further research is currently under way in our laboratory to determine whether improving selectivity and extending application to other alkenes and aldehydes is possible.

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