

RESEARCH NOTE

Highly Selective Fries Rearrangement over Zeolites and Nafion in Silica Composite Catalysts: A Comparison

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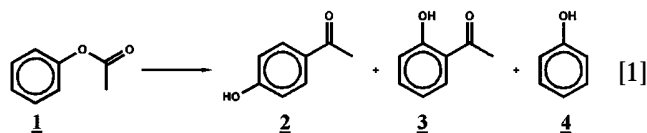
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Zeolites and acidic ion exchange resins are well known as potential heterogeneous catalysts for acid catalyzed reactions. Zeolites are a remarkable tool in catalysis as they offer reproducible well-defined surfaces. In addition, the microporous structure has a remarkable influence on the selectivity of a reaction and is sometimes tailored to suit the desired reactions. The isomorphous substitution can contribute a possibility to adjust the demanded acid strength for the reaction (1–3). Other substitutes for mineral acids provide strongly acidic sulfonic acid cation exchange resins (4, 5). For example, Nafion resin, a perfluorosulfonic acid resin, which is a copolymer of tetrafluoroethene and a perfluorosulfonylether derivative with a backbone similar to Teflon. The superacidity of such materials arises from $-\text{CF}_2\text{CF}_2\text{SO}_3\text{H}$ groups. The Hammett acidity has been suggested to be similar to concentrated sulfuric acid ($-\text{H}_0 \sim 12$) (6). Due to the perfluorocarbon backbone, the chemical inertness is very high for an organic resin. Until now a considerable number of reactions catalyzed by acidic Nafion resin have been studied (7, 8). Because of the very limited surface area ($0.02 \text{ m}^2/\text{g}$) of the pure resin and the very limited accessibility to the acid sites the activity in less polar solvents or in the gas phase reactions is reduced.

However, recently materials have been found with improved features (9). This has been achieved by entrapping nano-sized particles of Nafion in a high porous silica matrix. In this way the surface area of the new Nafion in silica composite catalyst is increased and most importantly the accessibility of the acid sites is increased. The activity of this new class of solid acids has as a result increased significantly, even in less polar solvents. For instance, in the dimerization of α -methylstyrene the composite catalysts generate a much higher reaction rate than the orig-

inal ion-exchange resin (10, 11). The isomerization of 1-butene is an example of a gas phase reaction, which is catalyzed by the pure Nafion resin to a less extent in contrary to the composite catalysts yielding high conversion (12).

It has been our intention to study the new materials in the Fries rearrangement of phenyl acetate, according to Eq. [1], and to compare it with competitive alternatives, such as zeolitic catalysts.



The Fries rearrangement of phenyl acetate **1** leads to hydroxyacetophenones **2**, **3**, which are very valuable precursors in the pharmaceutical industry to obtain, e.g. p-hydroxyacetanilid, which is used as a pain killer, also known as paracetamol (13). However, carrying out this reaction over heterogeneous catalysts has been not so successful until now, because of low selectivity and rapid catalyst deactivation (14). The zeolites studied in the present work are commercial products and were kindly provided by PQ-Corporation (H-Y (6); H-USY (70), Na-BEA (35), H-ZSM 5 (28)); the figures in brackets are the silica alumina ratios of the zeolites. Na-BEA is converted by a twofold ion-exchange with a tenfold excess of $2 \text{ N NH}_4\text{NO}_3\text{aq}$ at 80°C into the acid form and all of the zeolites have been calcined at 550°C for 8 h before use (15). The Nafion in silica composite catalysts contain 13 and 40 wt% Nafion, respectively. The porous silica matrix got a surface area of about $350 \text{ m}^2/\text{g}$ and an average pore size of about 10 nm. They were prepared according to literature (9). Pure Nafion resin is marked 100 wt%. All resins have been dried

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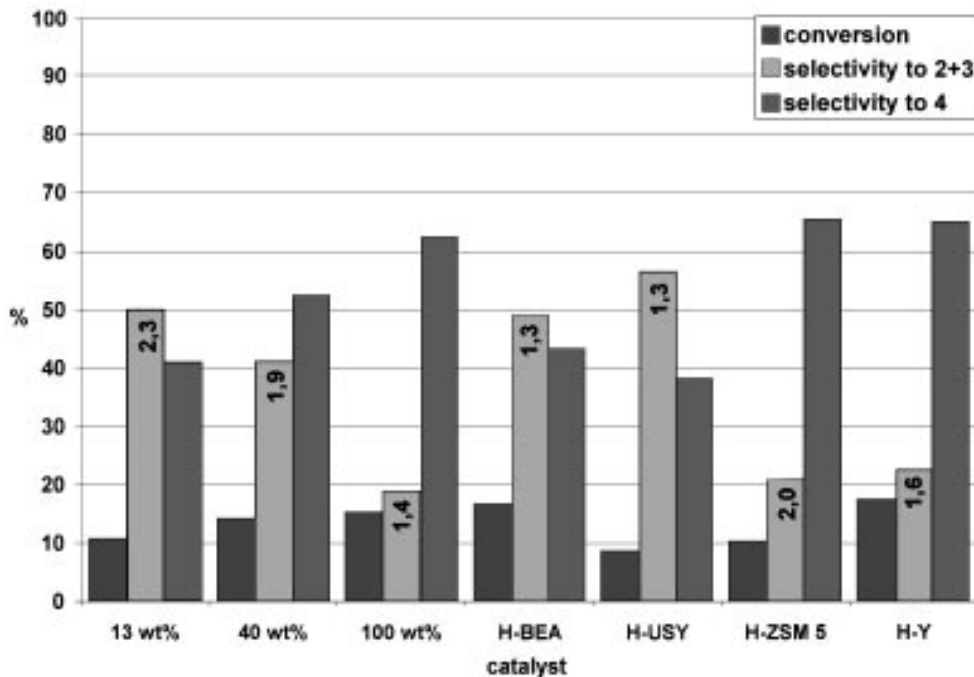
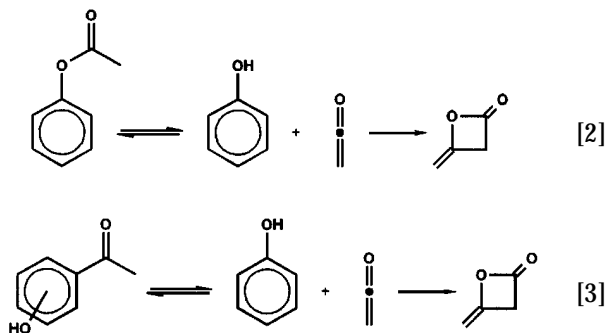


FIG. 1. Fries rearrangement of phenyl acetate (20 wt%) over different catalysts (2 wt%) in cumene as solvent at 150°C and normal pressure; the figures on the columns depict the ratio of 2 to 3.

before use for at least 4 h at 150°C in vacuum. Each solvent and reactant has been dried over molsieves. The reactions were carried out in batch reactors under dried Argon atmosphere at 100–200°C for 18 h. The reaction solution consisted of 78 wt% solvent, 20 wt% phenyl acetate, and 2 wt% catalyst. Results were determined by GLC analysis.

In Fig. 1 the results of the Fries rearrangement of phenyl acetate in the presence of various catalysts are depicted. The reactions are carried out in at 150°C and ambient pressure. The conversions are around 10 to 16% and the selectivity is in a range from 20 up to 56% as in the case of an ultrastable faujasite zeolite (H-USY (70)). An acylation of the solvent cumene can be excluded under these conditions. No acylated products could be obtained even with stronger acylation agents, as could be shown in some other experiments.

In comparison to the results of homogeneously catalyzed reactions such as in the presence of BF_3 or HF our findings are quite moderate. The main side product in this reaction is phenol. This could be formed via the decomposition of the starting ester or the deacetylation of the products. In both cases highly reactive keten is formed as the complementary decomposition compound, according Eqs. [2] and [3]. This keten reacts in consecutive irreversible reactions very unselectively to several products, in particular to diketen, resulting in low selectivity for the Fries rearrangement.



The consecutive products of keten also causes the rapid deactivation of the catalyst by coking. At a lower temperature <100°C the decomposition could be reduced; but at a reaction temperature of 100°C the conversion is very low.

By changing the solvent, in particular, using phenol, we found a tremendous change. The results shown in Fig. 2 have been obtained under the same reaction conditions described above for cumene as solvent. Now, in the presence of all catalysts tested selectivities of more than 50% are achieved. Using 13 wt% Nafion in silica composite catalyst a selectivity of more than 90% is obtained at a conversion of about 21%. Additionally, using the composite catalysts having 13 or 40 wt% of Nafion and over the H-BEA zeolite the conversion is considerably increased, too. In the case of H-BEA 76% selectivity at 41% conversion are achieved. Unfortunately, by reusing all the catalyst only

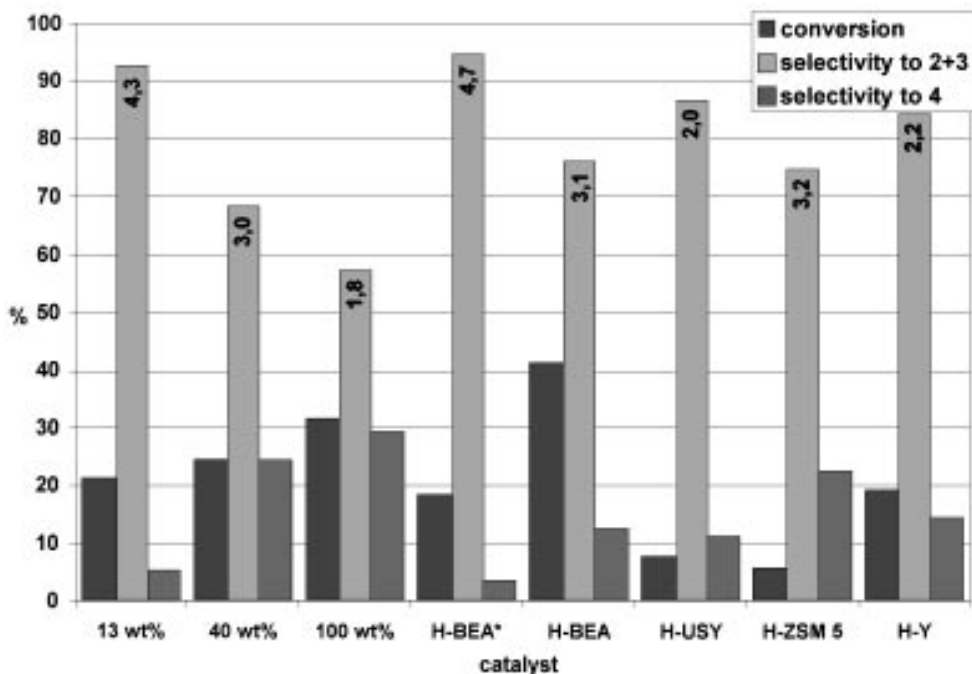


FIG. 2. Fries rearrangement of phenyl acetate (20 wt%) over different catalysts (2 wt%), and in the case of H-BEA*, also 1 wt% in phenol as solvent at 150°C and normal pressure. The figures on the columns depict the ratio of **2** to **3**.

traces of product could be obtained. The deactivation seems to be almost complete after reaction time. However, the catalysts can be reactivated. The Nafion in silica composite are regenerated by a washing procedure with acetone and nitric acid and the zeolites, by calcination in air at 550°C for 8 h.

It is assumed that in an excess of phenol the formed keten is caught immediately and the chemical equilibrium is shifted to the starting materials, according to Eqs. [2] and [3]. In this way the irreversible consecutive reactions out of keten do not take place. For this reason higher conversions and much higher selectivities are achieved.

Concerning the Nafion catalysts, the diagram shows that the conversion raises from 21% for the 13 wt% Nafion containing material to 31% for the pure Nafion resin. However, the pure material contains more than seven times Nafion resin than the composite material. In addition, both composites show a much higher selectivity, in particular the 13 wt% containing Nafion sample. This is likely due to the improved accessibility to the acid sites and rapid transport in and out of the catalyst reducing secondary chemistry.

In addition to the enhanced overall selectivity, the p/o ratio in the production distribution is enhanced, too. This effect is probably due to the higher polarity of phenol over cumene, which supports the formation of para-product **2**, as could already be shown by Jayat *et al.* (16).

It could be shown that the new Nafion in silica composite catalysts has improved the catalytic properties compared

to the original Nafion resin. They exhibit both higher activity and higher selectivity in the Fries rearrangement. In comparison to zeolitic catalysts, it is only the H-BEA zeolite which achieves a superior performance in this reaction with respect to conversion, but not to the overall selectivity under the chosen reaction conditions. However, at equal values of conversion, achieved by the use of only 1 wt% H-BEA, the selectivity (94.4%) over the zeolitic material is very high, too. Therefore, it can be emphasized that the zeolite H-BEA shows a better catalytic performance. In general, it has to be pointed out that the heterogeneously catalyzed Fries rearrangement can be much improved by using a suitable solvent, such as phenol.

We checked this behaviour for derivatives of phenyl acetate, too. As a result, the Fries rearrangement of p-tolyl acetate over the 13 wt% Nafion in the silica composite in p-cresol as the solvent is much more selective (82%) than in cumene as solvent (48%) at conversions of about 16 and 9%, respectively.

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