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The use of Nafion/silica composite catalysts for synthesis of fine chemicals

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ABSTRACT

An overview about different reaction types carried out with Nafion/silica composites is presented. The goal for all of the reactions is an improvement of known processes to fine chemicals in the field of pharmaceuticals, fragrances and vitamins. The use of Nafion/silica composites can provide better results, i.e. higher yields and selectivities, and allow conducting reactions under more environmentally friendly conditions.

1. Introduction

Because of environmental concerns, there is a strong interest in the use of solid acid catalysts as a replacement for classical homogeneously acting Lewis and Brønsted acid catalysts such as HF and H_2SO_4 [1–10]. Although these catalysts are effective, they lead to highly corrosive conditions and chemically reactive waste streams, resulting in high salt formation from neutralization of the used catalysts. As a consequence, purification of products and waste disposal is often difficult, cost intensive, and less environmentally benign.

A major challenge in this area is the development of highly active and selective heterogeneous acids for the replacement of the aforementioned homogeneous acid catalysts. A number of different types of solid acids, such as sulfated zirconia [1], heteropolyacids [2], zeolites [3,4,11–13] and perfluorinated resinsulfonic acids [5,6] has been investigated. Despite all these investigations the exact nature of the acid sites in these materials is still controversial [7]. There seems to be a need to fine-tune the catalytic properties for particular applications.

One of the better characterized solid acid catalysts is the group of the perfluorinated resinsulfonic acids, which have a similar acidity as 100% sulphuric acid. Nafion resin is known to catalyse a wide range of reactions [5,6], including olefin isomerisations, alkylations, acylations, oligomerisations, Fries rearrangements, condensations and benzylations.

Nafion is a copolymer derived from tetrafluoroethylene and perfluoro-2-(fluorosulfonylethoxy)propyl vinyl ether containing strongly acidic terminal groups $CF_2CF_2SO_3H$ formed after hydrolysis of the sulfonyl fluoride. The acid content is typically about 0.95 mequiv. g^{-1}. One major drawback of the commercially available material (Nafion NR 50) is the low surface area (0.02 $m^2\,g^{-1}$). This property results in low activity when non-swelling solvents or gas phase reaction conditions are applied.

To increase this activity, a new kind of solid Nafion catalysts have been developed. Thereby, a nanometer-sized colloidal dispersion of Nafion in polar solvents is mixed with a soluble silica precursor. This new generation of Nafion contains nanosized Nafion resin particles entrapped in a highly porous silica matrix. Those materials are called SAC (solid acid catalysts) followed by the Nafion loading, e.g. SAC 80 for 80% Nafion in the silica matrix. The BET surfaces of such materials are up to 20,000 times higher than the pure starting material Nafion depending on the preparation method. The pore size can be adjusted to values larger than 100 Å. Due to the better accessibility of the catalytically active acid sites, the activity of these composites is much higher than of pure Nafion. Furthermore, the higher thermostability of these new catalysts of up to 320 °C enables the possibility to work in the gas phase. There is no need of polar solvents for swelling the Nafion anymore allowing working in non-polar solvents. In this contribution, the performance of such catalysts will

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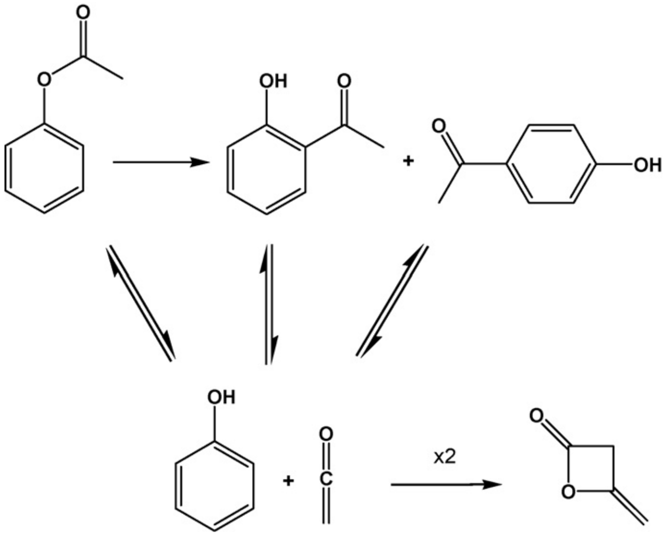
be compared to other heterogeneous catalysts for a selection of representative organic reactions.

2. Fries rearrangement for the synthesis of paracetamol

As shown in Scheme 1, aromatic esters are converted to aryl ketones in the Fries rearrangement. Lewis acids catalyse this reaction. A known technical application for this reaction is the synthesis of *p*-hydroxyacetanilide, better known as paracetamol or thylanol, which is used as an important painkiller produced in large quantities. Starting with phenyl acetate **1** using 70 °C in HF as solvent and catalyst, the reaction yields 90% of an isomer mixture of the hydroxyacetophenones **2** and **3**. The *para*/*ortho*-ratio is nine to one under these conditions [15]. The *p*-isomer **3** is then converted to the desired paracetamol via ammonoxidation and Beckmann rearrangement. For the last two reactions heterogeneously catalysed processes have already been developed. But up to now there has been no alternative process developed for the first step, although there are several known disadvantages of HF, such as toxicity and corrosiveness [16]. On the one hand, the activity of the heterogeneous catalysts is too low, on the other hand, they have low durability [17]. In contrast, the rearrangement of phenyl benzoate gives promising results with Nafion [18] as well as zeolites [19].

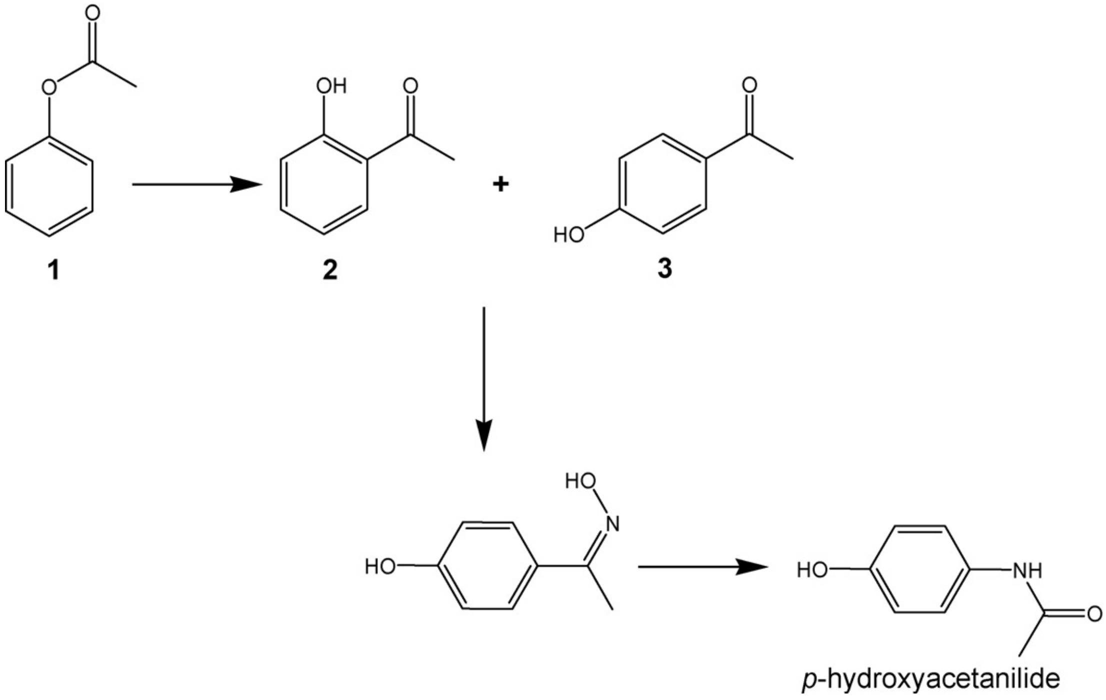
Nevertheless, the first attempts in the rearrangement of phenyl acetate **1** using Nafion/silica composites have been disappointing, and results were quite moderate when working in less polar solvents such as toluene or cumene. The main side product obtained is phenol. It could be formed via the decomposition of the starting material or the deacylation of the products as shown in Scheme 2. In both cases the highly reactive ketene is formed as a complementary decomposition product [20]. While the decomposition was a reversible process, the keten can react irreversible to a large number of products. One of this is the observed diketen shown in Scheme 2. The side products not only lower the selectivity of the desired product, they can also cause catalyst deactivation.



Scheme 2. Formation of side products in the Fries rearrangement of phenyl acetate.

A tremendous change in selectivity was found when cumene as solvent was replaced by phenol (see Fig. 1). It can be assumed that in the case of a high excess of phenol the chemical equilibrium is shifted to the starting material and the formation of ketene and its consecutive products is suppressed. For that reason, higher conversion and in particular higher selectivity for (**2** + **3**) could be achieved. Not only could the overall selectivity be increased, but also the isomer ratio was slightly higher. This influence of the solvent is already known in literature [21], there they found up to three times higher *p*/*o*-ratios in correlation to the choice of the solvent.

In Fig. 2, the results of the Fries rearrangement of phenyl acetate in the presence of various catalysts are depicted. Using pure Nafion resin (NR 50), the conversion of phenyl acetate is increased in comparison to SAC 13, but the selectivity to (**2** + **3**) is much lower.



Scheme 1. Fries rearrangement of phenyl acetate **1** to hydroxyphenones **2** and **3** as precursor for paracetamol (*p*-hydroxyacetanilide).

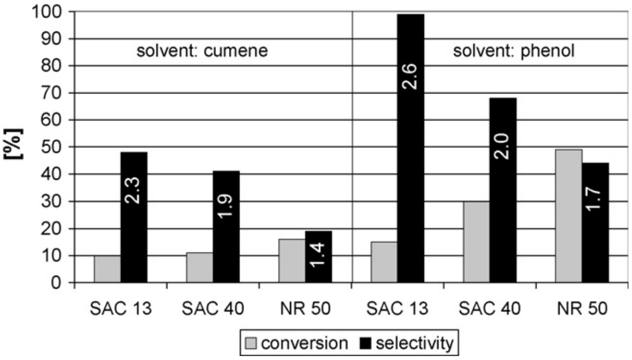


Fig. 1. Conversion of phenyl acetate and selectivity to hydroxyacetophenones (**2** + **3**), numbers on columns give **3**/**2**-(*p*/*o*)-ratio, achieved in different solvents using Nafion/silica resin and pure Nafion. Conditions: $T = 200\ ^\circ\mathrm{C}$; $t = 18$ h; solvent in 10 mol excess to reactant; 10 g reactant/1 g catalyst; slurry reactor.

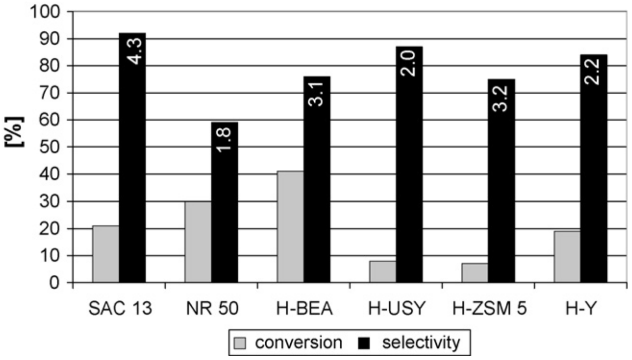


Fig. 2. Comparison of several catalysts in Fries rearrangement of phenyl acetate; selectivity to hydroxyacetophenones (**2** + **3**), numbers on columns give **3**/**2**-(*p*/*o*)-ratio. Conditions: $T = 150\ ^\circ\mathrm{C}$; $t = 18$ h; 20 wt% phenyl acetate in phenol; 10 g reactant/1 g catalyst; in a slurry reactor.

Also the *p*/*o*-ratio is more then doubled using the SAC 13 instead of NR 50.

It can be seen that zeolites with faujasite structure like HY and H-USY are less efficient. They show low conversion and low *p*/*o*-ratios. Also poor results are obtained with H-ZSM 5, although the isomer ratio is higher. HBEA shows interesting results. While here the selectivity is lower than in case of SAC 13, the conversion is nearly doubled. So it is a interesting catalyst for doing more optimisation.

In general it could be shown that heterogeneous catalysts can be a alternative in this reaction.

3. Pechmann reaction for the synthesis of coumarin derivates

Coumarin and its derivatives have attracted great interest because of their importance in synthetic organic chemistry. Many products containing subunits of coumarin are useful for diverse biological activity [22]. These compounds find their applications in pharmaceuticals, fragrances, agrochemicals and insecticides [23–25].

In the conventional production of coumarins based on phenol as starting material, concentrated sulphuric acid is used as catalyst [26]. This process causes formation of by-products, needs long reaction time and corrosion problems arise. For these reasons, there have been some attempts to find an alternative, environmentally benign heterogeneously acid catalysed synthesis route. Heterogeneous catalysts like zeolite H-BEA [27], Amberlyst 15 [28] and other solid acids [29] have been employed. Alternative catalysts for the Pechmann reaction in toluene are the Nafion/silica nanocomposites [30,31].

For the Pechmann reaction of resorcinol **4** and ethyl acetoacetate to produce 7-hydroxy-4-methylcoumarin **6** (Scheme 3) in toluene, Amberlyst 15, zeolites, pure Nafion and Nafion/silica composites were compared with each other. The results are shown in Fig. 6. The selectivities to the coumarin derivates are always higher than 80% for each used catalyst. But high conversion (>60%) could be only obtained in case of Nafion (both pure and silica composite) and Amberlyst 15. The zeolitic catalysts are less efficient. The highest yield with 96% was achieved by means of SAC 80.

In case of Nafion/silica composite catalysts two other remarkable effects could be observed. First, the amount of catalyst was reduced up to 50% and, second, the reaction time is reduced by 50%.

As seen in the Fig. 3 the activity of the composites is correlated with the amount of Nafion on silica. So the conversion of resorcinol rises from 68% for SAC 13 to 83% for SAC 40. The pure Nafion catalyst (NR 50) leads to a conversion of around 78%. This can be explained by the lower surface area ($<0.02\ \mathrm{m^2\ g^{-1}}$) of the NR 50.

To investigate the recycling of the catalyst, SAC 80 (the most active material for this reaction) was filtered off, washed with acetone and dried under ambient conditions for 2 h after each experiment. The results are illustrated in Fig. 4. As one can see, a drop in conversion after the first cycle of around 7% occurred. After another cycle the conversion drops again by 2%. In contradiction in the following experiments conversion remained constant at approximately 90% showing a selectivity of around 98%. So the

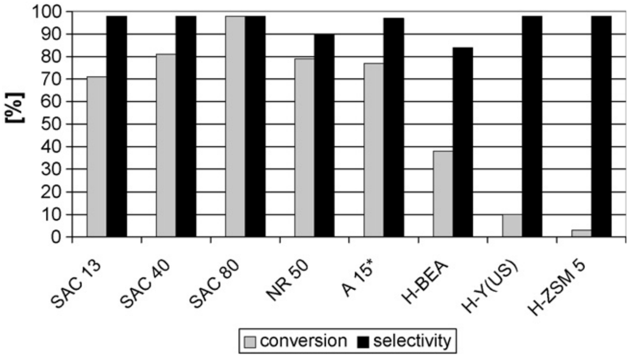
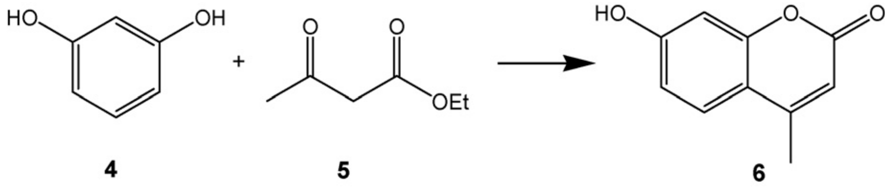


Fig. 3. Comparison of activity of different catalyst types for Pechmann reaction. Conditions: reflux temperature (110 °C); 0.5 g catalyst; $t = 22$ h; 10 mmol starting materials with ratio 1:1 in 10 ml toluene. *A 15: Amberlyst 15.



Scheme 3. Pechmann reaction of resorcinol **4** and ethyl acetoacetate **5** to produce 7-hydroxy-4-methylcoumarin **6**.

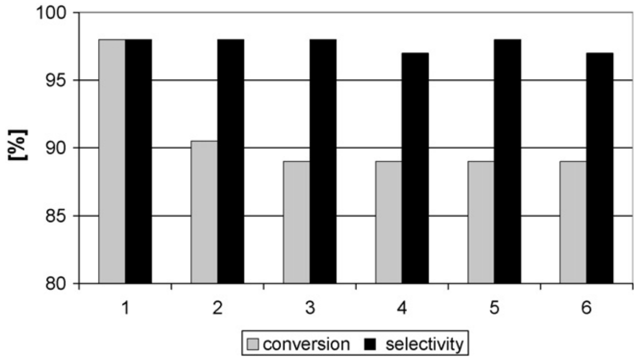


Fig. 4. Reusability of SAC 80 in Pechmann reaction. Conditions: $T = 110\,^{\circ}C$; $t = 2$ h; 0.5 g catalyst; 10 mmol starting materials with ratio 1:1 in 10 ml toluene.

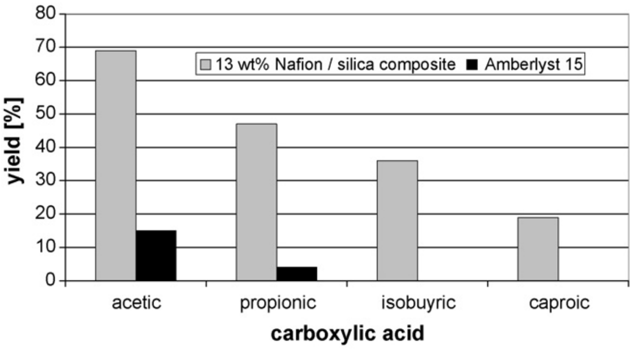


Fig. 5. Addition of different carboxylic acids to dicyclopentadiene. Conditions: $T = 80\,^{\circ}C$; $t = 2$ h; carboxylic acid/dicyclopentadiene 4:1, 10 wt% catalyst.

overall deactivation is low, although coke formation by aromatic resorcinol or coumarin was expected [32–34]. For the complete reactivation of the catalyst a washing procedure with diluted nitric acid or hydrogen peroxide solution was applied. The catalyst (0.5 g) is stirred in 20 ml of 15 wt% aqueous H_2O_2 for at least 2 h. After filtering of the catalyst is washed with water and dried at 120–150 °C in vacuum. Afterwards the original activity was fully obtained.

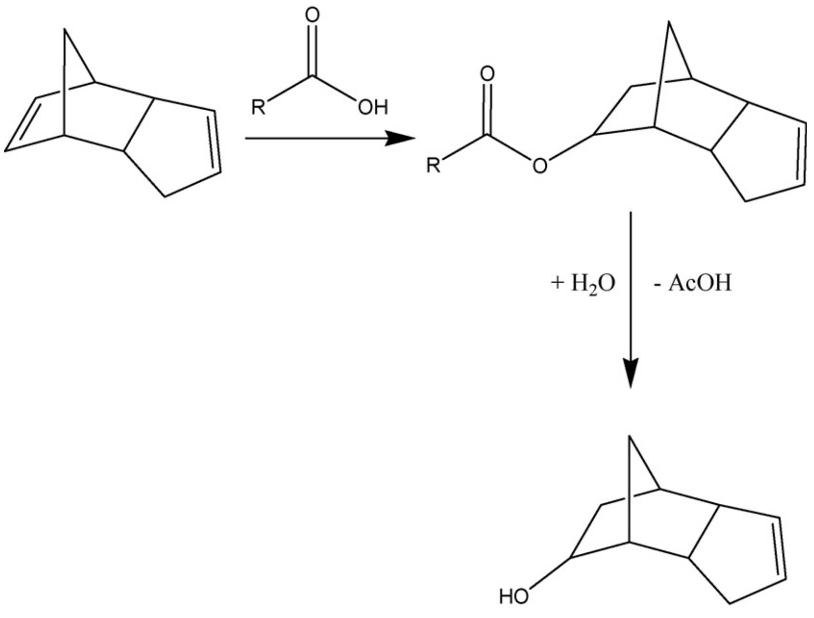
4. Addition of carboxylic acids to cyclic olefins

The addition of carboxylic acids to cyclic olefins such as dicyclopentadiene or naturally occurring terpenes yields compounds of industrial value [29]. An example for this is the addition of dicyclopentadiene **7** to carboxylic acids like acetic acid (Fig. 8). The resulting ester, verdyl acetate **8**, and the corresponding alcohol lead to starting compounds for the flavour and fragrance industry (Scheme 4). Using unsaturated acids as reagents, the resulting esters are compounds in the manufacturing of binders for polymer concrete [35].

The addition shows good results in case of homogeneous catalysis, using traditional mineral and Lewis acids, like BF_3 [36]. There are also some heterogeneous catalysts known. In this case, reactive olefins must be used to gain good results [37,38]. Using less reactive molecules, a high excess of carboxylic acid and a high amount of catalyst is needed [39]. An increase of temperature made the reaction rate higher but the selectivity is dropping [40].

Heterogeneous catalysts tested so far have shown unsatisfactory behaviour concerning the use of less active olefins [41–43]. Attempts to overcome these problems consisted in the application of high catalyst loadings or high reaction temperature, which in turn lead to problems with selectivity. Therefore, the highly active Nafion/silica composites were used for the addition of various carboxylic acids to dicyclopentadiene (Fig. 5). Under these reaction conditions, the SAC 13 is more active than the Amberlyst 15 in particular with respect to the number of acid sites. The ion exchange capacity of pure Nafion is about 0.89 mmol/g; the composite capacity has only around 0.12 mmol/g, whereas the Amberlyst provides 4.8 mmol/g.

The addition of carboxylic acids shows the trend, that higher molecular acids are less active in this reaction. In case of Amberlyst 15 the reaction of acetic and propionic acid results in the adduct. Using isobuyric or caproic acid the activity of Amberlyst 15 is too low to show any product. The higher active SAC 13 catalyses the reaction of all the mentioned acids, although there is a decrease of yield with higher molecular acids. So yields the reaction of acetic



Scheme 4. Addition of dicyclopentadiene to alkyl carboxylic acids like acetic acid leads to verdyl acetate and verdyl alcohol.

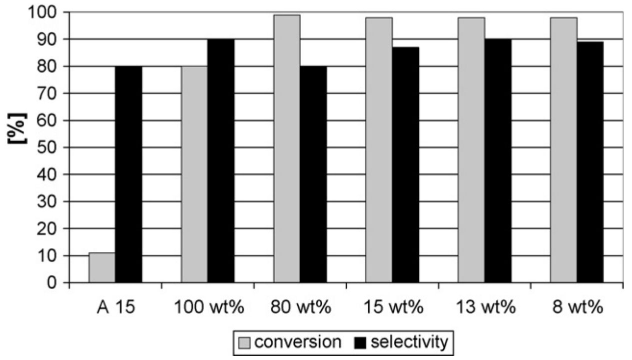


Fig. 6. Results with different Nafion loadings in comparison to Amberlyst 15 (A 15). Nafion/Silica composites with *X*% Nafion loading, 100 wt% is NR 50. Conditions: $T = 120\,^{\circ}\mathrm{C}$; $t = 2$ h; acetic acid/dicyclopentadiene 4:1; molar ratio reactant/SO_3H groups = 411; slurry reactor.

acid in 69%, propionic acid in about 48% and isobaric and caproic in 33 and 20% of the corresponding product.

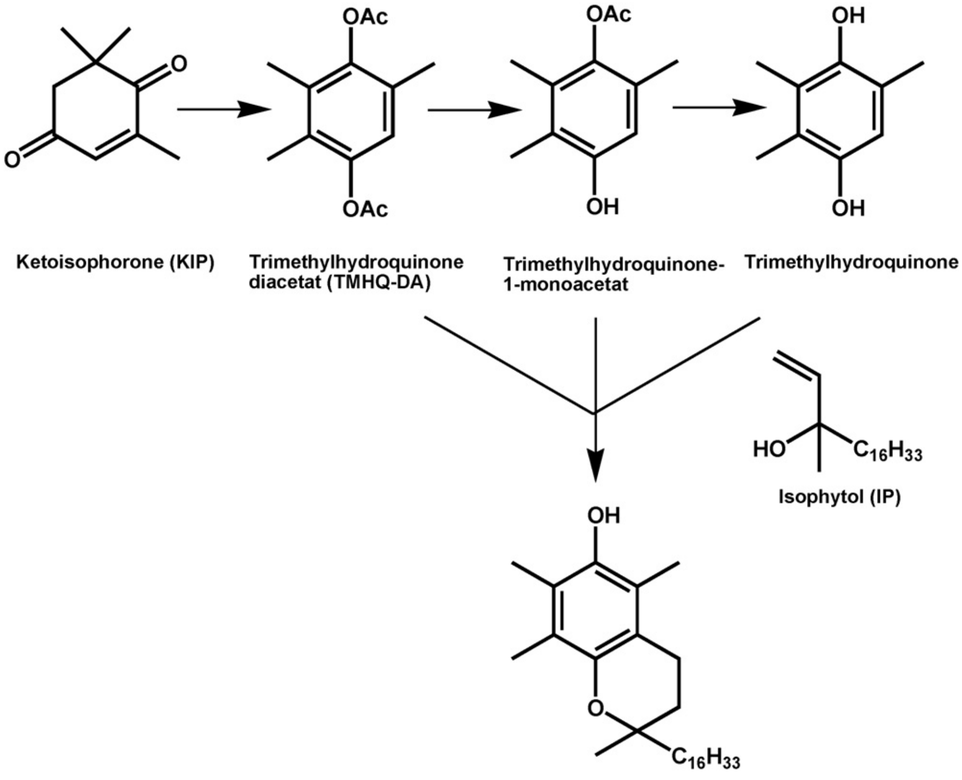
In Fig. 6 the results obtained over different composite catalysts with various Nafion loadings are illustrated. Total conversion is achieved over composite catalysts having Nafion content from 8 wt% up to 80 wt%. In contrast, the pure Nafion shows only 80% conversion. The reason for that is due to the low accessibility of the acid sites. In all cases the selectivities are 80% or higher. All composite catalysts are much superior over Amberlyst 15.

5. Condensation reaction for the synthesis of vitamin E

In the synthesis of vitamin E the step of ketoisophorone (KIP) to 2,3,5-trimethylhydroquinone diacetate (TMHQ-DA) as well as the conversion of TMHQ (obtained e.g. by saponification of TMHQ-DA) with isophytol (IP) to (all-*rac*)-α-tocopherol are acid catalysed [44–50] (Scheme 5).

The major interest of the present studies was related to the condensation of TMHQ with IP to form (all-*rac*)-α-tocopherol. A comparison of various Nafion/silica composites for this reaction is shown in Fig. 7. According to the varying activity an increase in the yield of tocopherol from 61% for SAC 05 to 73% for SAC 13 and 88% for SAC 40 can be observed. The higher activity is caused by the higher number of accessible strong acid centers, which is correlated to the increased Nafion amount in the composites. With SAC 80 a decline of the yield is noted. This reduced yield is corresponding to a loss in selectivity. The reason for that could be that the formation of higher molecular by-products is favoured by using the very active catalyst SAC 80. Another disadvantage of SAC 80 is the fast deactivation in strong polar media such as propylene carbonate at 100 °C. The lower stability of SAC 80 compared to SAC 40 can be explained by the lower silica amount. For further optimization SAC 40 was used. In Fig. 8 it can be seen that already 0.6 wt% catalyst is sufficient to reach yields higher than 80%.

Consequently, the SAC 40 material produced by the sol–gel technique [40,41] has, in contrast to the supported Nafion/SiO_2 or the pure Nafion, improved stability with the same or even higher catalytic performance in polar propylene carbonate. This is desirable particularly since the results obtained in other solvents are clearly inferior (see Table 1). Furthermore, the recycling of SAC 40 was investigated (Fig. 9). A decrease in the yield of tocopherol from 88 to 78% after the second run is observed. In the next run the conversion decreases by additional 20%. For the reactivation of the catalysts a washing procedure with oxidizing agents can be applied. The reactivation process is the same as explained in the Pechmann reaction chapter.



Scheme 5. The synthesis of vitamin E.

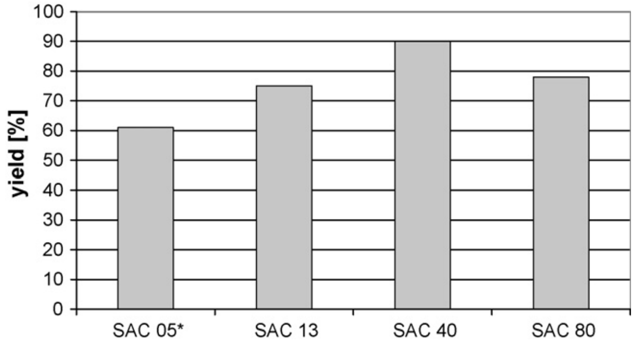


Fig. 7. Yield of tocopherol with different Nafion loadings. Conditions: $T = 100\,^{\circ}C$; $t = 1$ h (*14 h); 49.5 mmol TMHQ; 33 mmol IP; 1 g (0.9 wt%) catalyst; propylene carbonate/heptane (50 ml/50 ml).

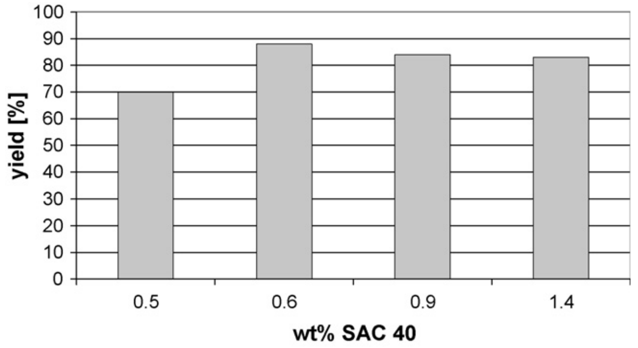


Fig. 8. Yield of tocopherol with different amounts of SAC 40. Conditions: $T = 100\,^{\circ}C$; $t = 1$ h; 49.5 mmol TMHQ; 33 mmol IP; propylene carbonate/heptane (50 ml/ 50 ml).

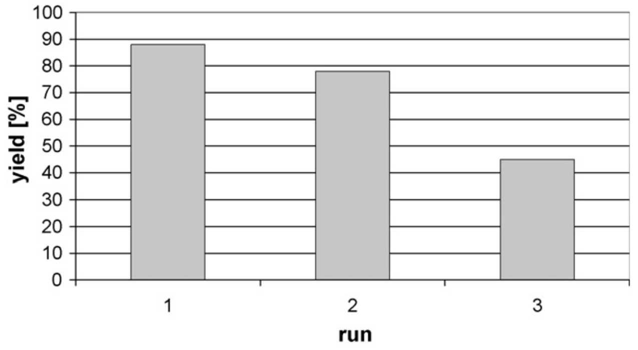


Fig. 9. Recyclability of SAC 40. Conditions: $T = 100\,^{\circ}C$; $t = 1$ h; 49.5 mmol TMHQ; 33 mmol IP; 1 g (0.9 wt%) SAC 40; propylene carbonate/heptane (50 ml/50 ml).

Table 1
Influence of solvent in tocopherol synthesis

Catalyst	Solvent (50 ml)	Catalyst/IP (g/g)	Yield (%)
Nafion NR 50	Toluene	0.17	75
15 wt% Nafion/SiO_2	Toluene	0.10	72
Nafion NR 50	Propylene carbonate/ heptane	0.17	92
15 wt% Nafion/SiO_2	Propylene carbonate/ heptane	0.10	92
15 wt% Nafion/SiO_2	Butyl acetate	0.10	78
15 wt% Nafion/SiO_2	γ-Butyrolactone	0.10	72

6. Conclusions

Due to environmental concerns, there is an urgent need to replace homogeneous Lewis and Brønsted acids used as catalysts for organic reactions by heterogeneous materials. One group of these materials are perfluorinated resinsulfonic acids, e.g. Nafion. These ion exchange resins can display very high acidity. Nevertheless, the low surface areas of the pure materials limit their usability. Nafion/silica composite materials offer an interesting alternative. These contain nanosized Nafion particles within a silica matrix and display high surface area and good thermostability.

Here, we report the usage of Nafion/silica composite materials in four different organic reactions, all of which are important in the production of pharmaceuticals, fragrances and vitamins.

The Fries rearrangement of phenyl acetate leads to valuable precursors for *p*-hydroxyacetanilid, also known as paracetamol. A comparison of different catalysts showed that, when using phenol as a solvent for this reaction, a Nafion/silica composite with 13 wt% silica (termed SAC 13) showed a higher activity in the reaction than all other tested heterogeneous catalysts, with the exception of HBEA zeolite. The composite material was even more active than pure Nafion NR 50.

Coumarin derivates are used in many fine chemical products. They can be obtained by reactions of the Pechmann type. We compared the activities of three different zeolites, Amberlyst 15, Nafion NR 50, and four Nafion/silica composites in the Pechmann reaction of resorcinol and ethyl acetoacetate. The highest yield of the desired product was obtained with the Nafion/silica composite SAC 80. The composite could be reused, and complete activity was recovered after washing with diluted nitric acid or a hydrogen peroxide solution.

The addition of carboxylic acids to cyclic olefins is a reaction that is important in the production of various terpenes for the fragrance industry. We compared the catalytic activity of Nafion and Nafion/silica composite materials in the addition of various carboxylic acids to dicyclopentadiene to that of Amberlyst 15. All of the composite materials showed superior activity.

Various Nafion/silica composites were investigated for their activity in the condensation of 2,3,5-trimethylhydroquinone with isophytol, an important step in the synthesis of vitamin E. The highest yield was obtained with SAC 40. The catalyst's activity decreased when reused, but the initial activity could be recovered completely by washing with oxidizing agents.

In the reactions listed here, Nafion/silica composite materials have been proven to be highly active and stable catalysts for a wide variety of acid-catalysed reactions.

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