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Addition of Carboxylic Acids to Cyclic Olefins Catalyzed by Strong Acidic Ion-Exchange Resins

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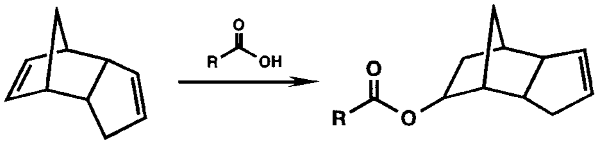
The esterification of several cyclic olefins with saturated and unsaturated carboxylic acids has been studied over highly dispersed strongly acidic ion-exchange resins based on Nafion, where the Nafion is entrapped within a porous silica matrix. Over these new catalysts the accessibility of the acid sites is much improved, in comparison to the original material. The activity has been compared to that of Amberlyst 15. The Nafion-based catalyst materials are superior to the weaker acidity Amberlyst catalysts when less active olefins are used and especially at low temperatures. © 1999 Academic Press

Key Words: **esterification; heterogeneous catalysis; Nafion; silica; Amberlyst; ion-exchange resins.**

INTRODUCTION

The esterification of cyclic olefins with carboxylic acids, such as dicyclopentadiene or naturally occurring terpenes, yields compounds of industrial value (1). For instance, the esterification of dicyclopentadiene with saturated carboxylic acids, such as acetic acid, leads to a starting material for the flavor and fragrance industry, as well as the resulting alcohols in consecutive hydrolysis (2). By using unsaturated carboxylic acids as nucleophiles, the resulting esters are also useful compounds in the manufacture of binders for polymer concrete (3).



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The esterification is known to be catalyzed quite well by homogeneous catalysts (4). Several traditional catalysts such as BF_3 render the desired compounds in high yield (5). However, toxicity, corrosion, and difficult separation procedures of the catalysts are well known disadvantages of the homogeneously catalyzed reaction in industrial applications. Up to now several heterogeneous catalysts have been found which show good performance in this reaction (6). However, only very reactive olefins are effectively catalyzed heterogeneously (7). In the case of less active olefins, in order to realize high yields a very high carboxylic acid olefin ratio or very high catalyst loading is needed (8). Unfortunately, raising the reaction temperature to enhance the reaction rate causes a decrease in selectivity.

Now, we have studied Nafion/silica composite catalysts in this kind of reaction, since former results showed that this material is much more active than the original pure acidic ion-exchange resin Nafion NR 50 (9–13). This new material can be considered as nano-sized Nafion particles entrapped within a porous silica matrix. Thus, the surface area of the dispersed Nafion in the composite is much larger than that of the original Nafion material, resulting in a much improved accessibility of the acid sites on the catalyst. In addition, this composite can be used in reaction media which have been unfavorable so far. Nonpolar solvents do not cause swelling of the ion-exchange resin and, as a result, reaction rates are rather low due to the worse accessibility of the acid sites. The same pattern is also found in reactions carried out in the gas phase. This disadvantage is removed by the rigid matrix of the silica, so that the composite can be used as a catalyst, even in nonpolar solvents, as well as in gas-phase reactions. The composites can be obtained by simple sol–gel coprecipitation of nano-sized Nafion particles and a silica source. The resulting material contains uniformly dispersed Nafion particles.

We compared composites containing different amounts of Nafion catalyst with the original material and with Amberlyst 15, a well-known macroreticular ion-exchange resin, which achieves remarkable results in several acid catalyzed reactions (14).

EXPERIMENTAL

In batch experiments the olefinic compound was added to a mixture of the catalyst and the carboxylic acid which was preheated in a two necked glass flask, equipped with a reflux condenser and a magnetical stirrer. The stirring speed was adjusted so high that further increasing did not

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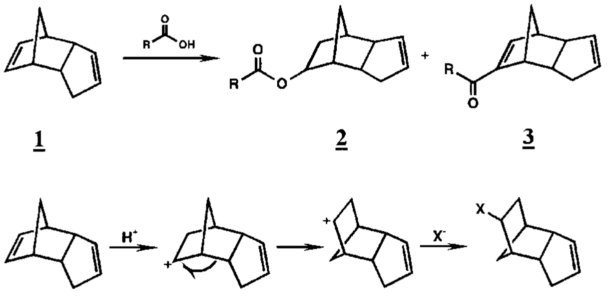
lead to higher conversions. The carboxylic acids, the olefinic compounds and the Amberlyst 15 resin (20–60 mesh) were purchased from Fluka and used without further treatment. Only dicyclopentadiene has been freshly distilled and stored under argon before use. The composite catalysts have been prepared as described previously (6). The average porous diameter ranges between 10 and 20 nm. The Nafion resin content was varied from 8 to 80 wt% and the catalyst was dried at 140°C for 4 h under vacuum and sieved to similar partical sizes as the Amberlyst resin. The Amberlyst 15 resin, too, was dried for 4 h under vacuum, but at 80°C. Products were analyzed by GLC and analyzed by authentic samples synthesized according to the literature.

RESULTS AND DISCUSSION

Esterification of Dicyclopentadiene with Saturated Acids

During the acid-catalyzed esterification of dicyclopentadiene **1**, a rapid Wagner–Meerwein-type rearrangement occurs simultaneously, according the reaction scheme [2]. As a result, the ester compound contains exclusively the dicyclopentenyl component in the exo-form. Especially, at elevated reaction temperatures the selectivity to **2** decreases due to formation of the main side product **3**.

Figure 1 shows the esterification of different saturated carboxylic acids with dicyclopentadiene. In all depicted experiments the carboxylic acid/dicyclopentadiene molar ratio is about 4 and the amount of catalyst is 10% by weight of dicyclopentadiene at a reaction temperature of 80°C. In this reaction the Nafion/silica composite catalyst is more active, compared to the Amberlyst resin, in particular with respect to the amount of acid groups on the resin. The ion-exchange capacity of pure Nafion is about 0.89 mmol/g; thus the composite capacity is only about 0.12 mmol/g; whereas the Amberlyst resin provides 4.8 mmol/g. As a result, in the case of acetic acid as nucleophile the turnover number (TON) of the sulfonic acid groups in the Nafion-based material are two magnitudes higher than the ones of the Amberlyst material. By using carboxylic acid with longer chain-length the difference in activity between the Nafion/silica composite and the Amberlyst seems to be even higher. With propionic acid the Amberlyst catalyst renders only just about 5% yield, and with both isobutyric and caproic acid only traces of the products are obtained. The Nafion-based material leads to more than a 45% yield by using propionic acid and almost 20% for caproic acid.



[2]

Carrying out experiments with equal ratios of starting material **1** to the sulfonic acid group of the specific catalysts reveals the same pattern as obtained in the experiments described above.

Figure 2 shows the results obtained over some Nafion/silica composite materials having different amounts of Nafion within the material and for comparison over the Amberlyst ion-exchange resin, too. Over all Nafion/silica

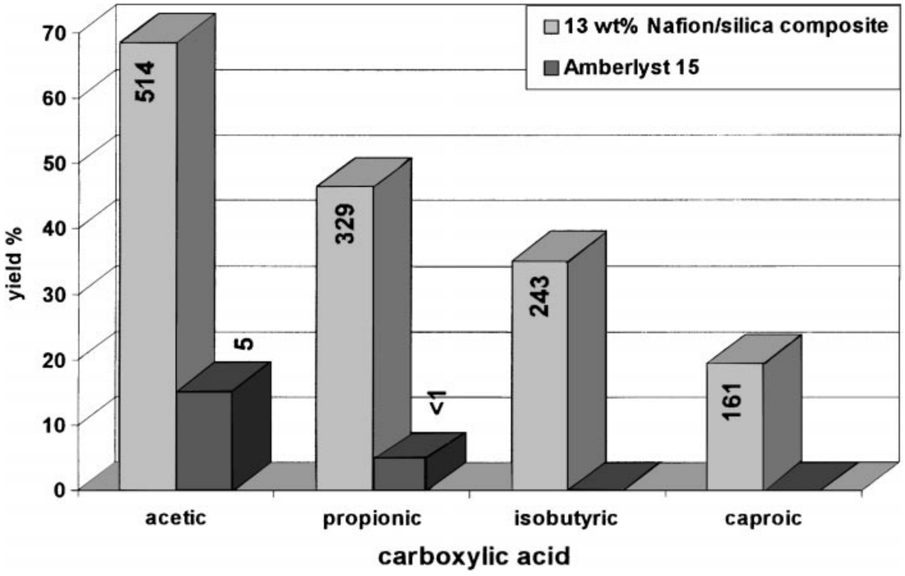


FIG. 1. Esterification of **1** with different carboxylic acids over 13 wt% Nafion/silica composite (SAC 13) and Amberlyst 15; the figures on the columns depict the TON mol(converted starting material)/mol(acid group).

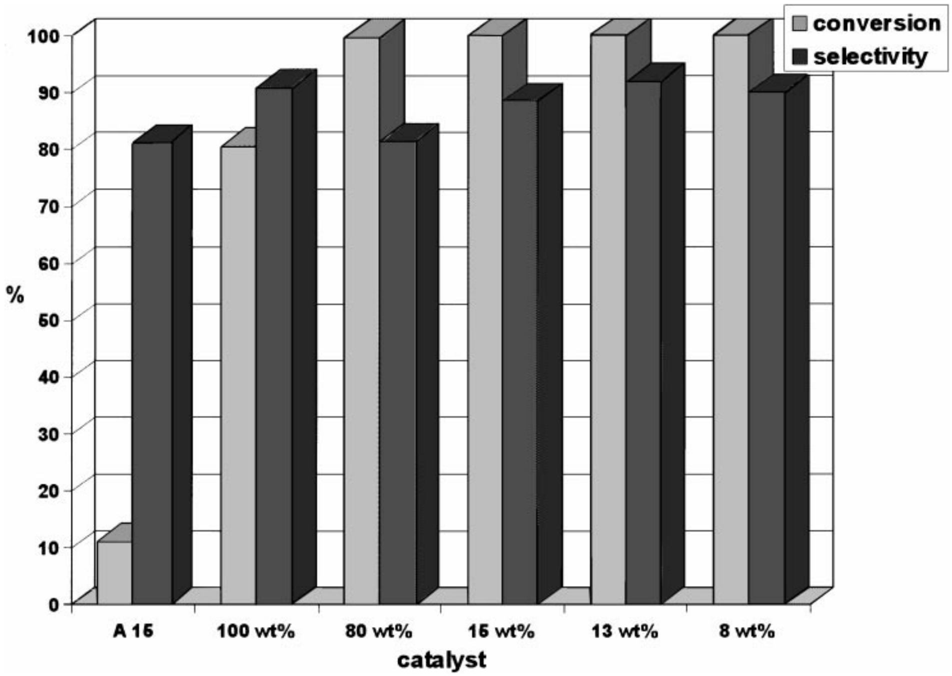


FIG. 2. Esterification of **1** with acetic acid over Nafion/silica composite catalysts with different amounts of Nafion within the catalysts and over Amberlyst A 15 ion-exchange resin; reaction temperature 120°C, $t = 2$ h, acetic acid in 4 molar excess, molar ratio of **1** to -SO_3H group = 411.

composite catalysts complete conversion is always achieved independently of the amount of Nafion resin within the material. In contrast, a conversion of only about 80% is obtained over the pure polymer. Again, the Amberlyst material achieves only a poor conversion of about 12%.

It seems, due to the very high activity of the Nafion/silica-based catalysts that these reaction conditions are not suitable to observe any differences in activity between the various Nafion/silica materials. In the case of the composites, for example, with a starting material to sulfonic acid group ratio of about 1000 reveals complete conversion over all composites, too.

Esterification of Dicyclopentadiene with Unsaturated Acids

By using unsaturated acids as a nucleophile a reaction temperature of about 120°C may cause polymerization of the products. So the reaction temperature was therefore reduced to about 80°C. A similar pattern is observed by using acrylic acid as a nucleophile as shown in Fig. 3. At a starting material to sulfonic acid group ratio of 750 about

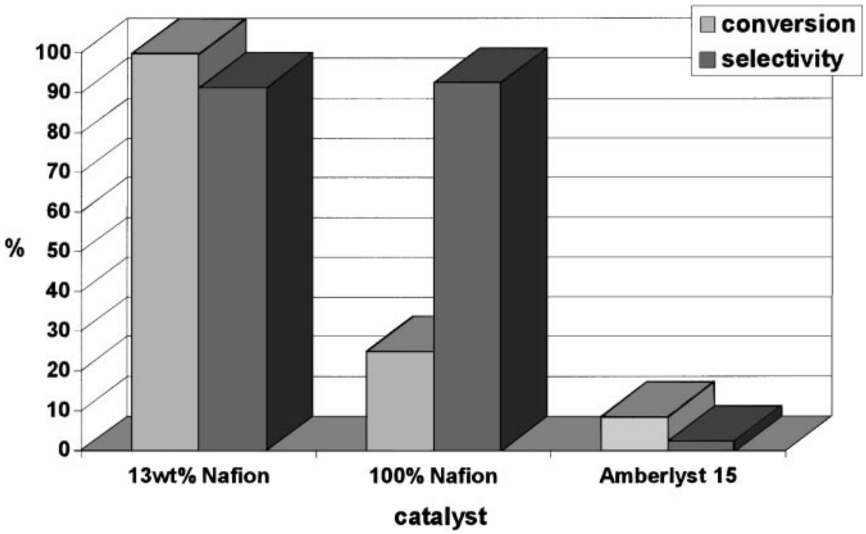


FIG. 3. Esterification of **1** with acrylic acid, acrylic acid in fourfold molar excess; $T = 80°C$; molar ratio educt/-$SO_3H = 750$; $t = 4$ h.

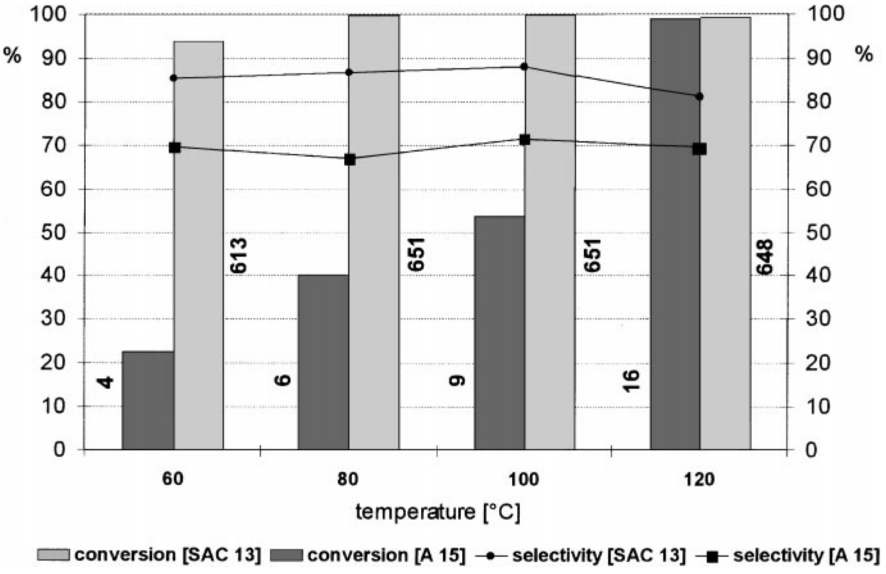


FIG. 4. Esterification of **1** with acrylic acid, acrylic acid in fourfold molar excess; 10 wt% catalyst; $t = 4$ h.

91% yield of the esterificated product is obtained over the composite catalyst, whereas by using Amberlyst 15, less than 5% of the desired product is achieved. The difference in activity between the composite and the original material is especially striking, in view of the higher ratio of starting material to sulfonic acid group. In addition, the acrylic acid seems to be much more active in this reaction than acetic acid. This difference could be caused by the higher acid strength of acrylic to acetic acid.

Since the difference of the ion-exchange capacity of the composite material to the Amberlyst resin is quite high experiments have also been carried out with the same catalyst loading with respect to the weight of the catalyst. In Fig. 4 the catalyst loading is 10 wt% with respect to the amount of the starting material. In addition, the experiment has been carried out at different reaction temperatures in order to determine the temperature which is sufficient for a complete conversion over the Nafion-based catalyst.

At 80°C the Nafion-based material still shows complete conversion and is much superior to the Amberlyst resin, also with high selectivity which is about 87% and 67%, respectively. Actually, the conversion over the Amberlyst resin is increased to 40% but the amount of catalyst is about 48 times higher than in the run shown in Fig. 3.

For the composite at 60°C the conversion drops to about 94%, whereas the Amberlyst resin achieves still only 23%. At all temperatures the selectivity is generally higher by using the Nafion-based catalysts. Again, the turnover numbers of the Nafion-based material are again two magnitudes higher.

Figure 5 shows that even at a lower molar excess of acrylic acid to dicyclopentadiene the conversion remains on a very high level. Moreover and surprisingly, the selectivity is maintained at more than 90%. Even at only a twofold molar excess of acrylic acid the reaction is still complete. Finally, when an equimolar ratio of the reactants is used the conversion drops to 48%.

By using methacrylic or dimethylacrylic acid the difference in activity between both catalysts remains high despite the fact that actually the Nafion-based does not render complete conversion anymore as shown in Table 1. In this case selectivity is decreased to 81% for methacrylic acid, which is likely due to polymerization reactions caused by the higher reaction temperature.

Esterification of Norbonene and Norbonadiene

The esterification of norbonene **4** and norbonadiene **6** has been carried with acrylic acid as the nucleophilic compound over both catalysts, the Nafion/silica catalyst and the Amberlyst resin. The reaction conditions used were the same as before but the temperature has been varied. In

TABLE 1

Esterification of 1 with Methacrylic (Runs No. 1–4) and Dimethylacrylic (Runs No. 5, 6) Acid, Carboxylic Acid in Fourfold Molar Excess; 10 wt% Catalyst; $t = 4$ h

Run no.	Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)	TON
1	SAC 13	120	93	81	608
2	Amberlyst 15	120	26	50	4
3	SAC 13	100	87	82	569
4	Amberlyst 15	100	9	44	1
5	SAC 13	120	40	88	262
6	Amberlyst 15	120	12	85	2

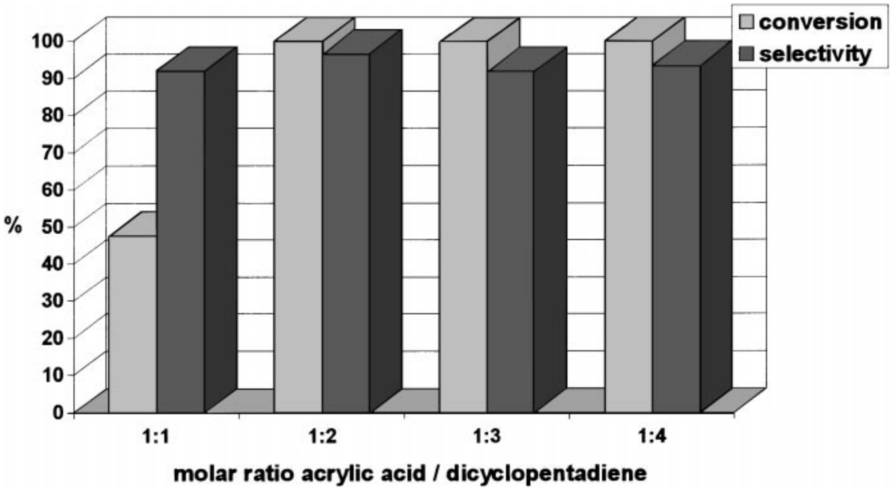
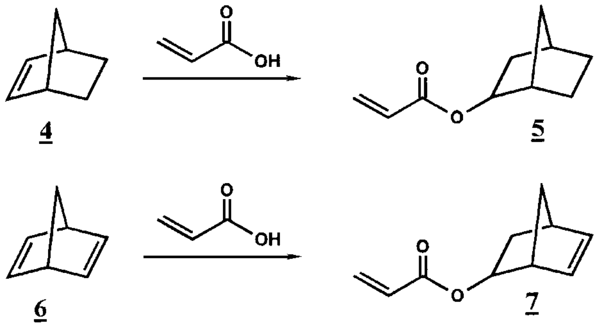


FIG. 5. Esterification of **1** with acrylic acid with different molar ratios, $T = 80°C$, $t = 2$ h, 10 wt% catalyst [SAC 13].

contrast to dicyclopentadiene **1** in this reaction both isomers, the exo- and endo-orientated, were formed.



[3]

Now the results, shown in Table 2 reveal at a reaction temperature of 80°C a similar activity of the Amberlyst and the Nafion-based catalysts are found when using norbonene as the olefinic compound. Both catalysts achieve virtually complete conversion and very high selectivities of more than 98%. However, by using norbonadiene **6** as the olefinic compound the maximum operation temperature must not exceed much above 40°C; otherwise spontaneous polymerization occurs. At this reaction temperature the Nafion-based catalyst reveals higher activity again.

TABLE 2

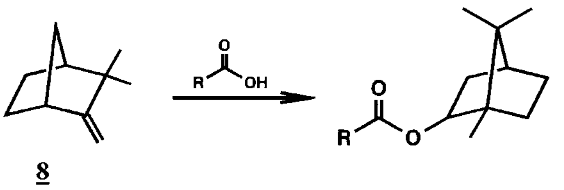
Esterification of 4 (Runs No. 7, 8) and 6 (Runs No. 9, 10) with Acrylic Acid, Acrylic Acid in Fourfold Molar Excess, 10 wt% Catalyst, $t = 2$ h

Run no.	Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)
7	SAC 13	80	97	98
8	Amberlyst 15	80	96	98
9	SAC 13	40	62	90
10	Amberlyst 15	40	15	94

Thus, in these reactions the Amberlyst resin may be an alternative catalyst to the Nafion-based material when the reaction temperature is allowed to be adjusted high enough. When there are limitations due to polymerization, the Nafion-based material seems to be superior again.

Esterification of Terpenes

Under standard conditions and temperatures from 40°C to 100°C limonene and α-pinene were esterificated with acetic and acrylic acid, respectively, over the Amberlyst resin, as well as the Nafion composite. The conversion is high; however, the reaction is very unselective and no distinct main product is obtained. It seems that both terpenes rearrange to several different products before the final esterification takes place.



[4]

Using camphene **8** as a starting material much better results are obtained (reaction scheme [4]).

Both, the composite catalyst SAC 13 and the Amberlyst resin A 15 show high activity and high selectivity in this reaction even at a low temperature of about 20°C. This olefinic compound seems to be so reactive as to render high conversion independently of the acid strength of the catalyst. This could be due to the terminal double bond and to the very stable carbo-cation formed by protonation.

TABLE 3

Esterification of Camphene 8 with Acetic (Runs No. 11, 12) and Acrylic Acid (Runs No. 13–16) at Different Temperatures, Carboxylic Acid in Fourfold Molar Excess, 10 wt% Catalyst, $t = 2$ h

Run no.	Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)
11	SAC 13	80	88	87
12	Amberlyst 15	80	88	88
13	SAC 13	60	94	92
14	Amberlyst 15	60	93	85
15	SAC 13	20	94	87
16	Amberlyst 15	20	93	89

CONCLUSIONS

In the esterification of all studied cyclic olefins the Nafion in silica composite catalysts are much more active than the original pure resin and than the Amberlyst A 15 resin, too. Even at comparatively low temperatures the composite materials achieve high conversion. This is due to the much improved accessibility of the acid sites and to their higher acid strength. Although the ion-exchange capacity of the 13 wt% Nafion-containing material (SAC 13) is more than 40 times lower than Amberlyst, the resulting activity per mass of the catalyst is much superior to the Amberlyst resin. Only, when very reactive olefins are used do all catalysts reveal high reactivity.

ACKNOWLEDGMENT

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