Journal of Catalysis **188,** 230–232 (1999)
Article ID jcat.1999.2656, available online at http://www.idealibrary.com on IDEAL®

RESEARCH NOTE

Nafion/Silica Composite Material Reveals High Catalytic Potential in Acylation Reactions

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Received May 26, 1999; revised August 2, 1999; accepted August 4, 1999

Friedel–Crafts acylations are very important reactions for the synthesis of many organic substances of great interest in the field of fine chemistry (1). However, the traditional catalysts, such as $AlCl_3$, BF_3, and HF, lack in several respects. Their use in more than stoichiometric quantities combined with their toxicity and troublesome working-up procedures cannot be called sustainable anymore (2, 3).

Consequently, several attempts have been made to replace the traditional materials by heterogeneous catalysts (4–6). Although success has been noteworthy, in quite a number of cases the lower activity of heterogeneous catalysts has restricted applications. Zeolites are quite promising catalysts for the acylation of activated aromatic compounds, such as anisole (7–9). However, when using less activated aromatics at high temperatures, long reaction times and large amounts of catalysts are needed to achieve reasonable acylation. These reaction conditions often lead to a loss in selectivity. In addition, the use of highly reactive carboxylic acid halogenide compounds as acylating agents, as well as the anhydrous HCl, which is produced during the reaction, may remove the aluminum species from the zeolite framework (10).

Alternatively, acid-treated clays may be more active than zeolitic structured materials though the problem of stability of the catalysts during the reaction still remains (11).

However, just recently it was shown that even nonacidic materials such as graphite exhibit encouraging activity in the catalysis of acylation reaction, when carboxylic acid halogenides are used in combination with active aromatic compounds (12).

In this paper we will show that Nafion/silica composite catalysts serve as promising catalysts for the acylation of even less active aromatic compounds. These very strong solid acids, which can be made by entrapping highly dispersed nanosized Nafion particles within a silica matrix, have been reported to have a high catalytic potential in several other reactions (13–17). These catalysts contain the advantages of both components, the acidic strength of the Nafion resin and the simple accessibility of the high surface area of silica (18). The combination results in high catalytic activity at both moderate reaction temperature and low catalyst loadings, which often guarantees high selectivity to the product desired.

In the batch experiments 2.5 g of the carboxylic acid chloride were added to a mixture of 0.5 g catalyst and 10 or 20 g aromatic compound, which was preheated in a two-necked glass flask equipped with a reflux condenser and a magnetic stirrer. The reactions were carried out in a dry and inert argon atmosphere. Both the carboxylic acid chlorides and the aromatic compounds were purchased from Fluka and used without further treatment. The aromatics were dried and stored under argon before use. The Nafion resin (Nafion NR 50) was kindly provided by DuPont. The composite catalyst (SAC 13) contained 13 wt% nanosized Nafion particles in a porous silica matrix and was prepared as described previously (18). The average pore size diameter ranged between 10 and 20 nm. The Nafion resin and the composite material were dried at 413 K for 4 h under vacuum before use. Products were analyzed by GLC and identified by authentic samples synthesized according to the literature and by GC-MS.

The acylation of anisole with phenylacetic acid chloride **1** and phenylpropionic acid chloride **2** is catalyzed by pure Nafion resin NR 50 and the Nafion/silica composite material SAC 13 (see Eq. [1] in Scheme 1). Table 1 shows the results performed at different reaction temperatures and varying ratios of anisole **3** to the acid chlorides **1**, **2**. According to former results, it is to be expected that the composite material is more active than the original acidic resin (14–17). By using **1** in the presence of NR 50, the conversion increases from 46 to 77% by increasing the temperature (runs 1–3,

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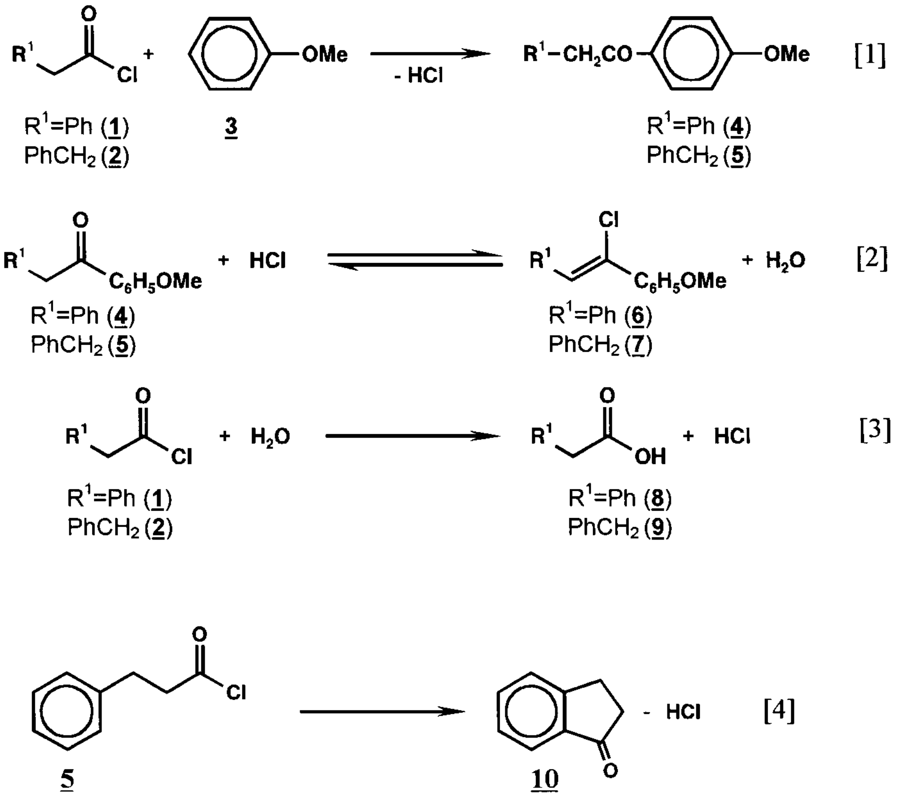
0021-9517/99 $30.00



SCHEME 1

Table 1), whereas the composite material achieves 71 to 100% conversion during the same rise in temperature (runs 5–7, Table 1), although it contains only 13% of the Nafion resin. Surprisingly, the selectivity to the desired product **4** steadily rises with increasing temperature and conversion. In the case of NR 50 the selectivity rises from 77% at 333 K to 89% at 373 K. This behavior will be explained by a closer view of the side reactions.

TABLE 1

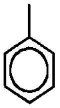
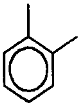
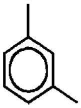
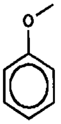
Acylation of Anisole by 1 and 2 Catalyzed by Original Nafion Resin NR 50 and Nafion/Silica Composite SAC 13

Run no.	Acid cloride	Temperature (K)	mass ratio **3**/**1**, (**2**)	Catalyst	Conversion (%)	Selectivity to **4**	Selectivity to **5**
1	1	333	4	NR 50	46	77	
2	1	353	4	NR 50	68	87	
3	1	373	4	NR 50	77	89	
4	1	373	8	NR 50	60	97	
5	1	333	4	SAC 13	71	81	
6	1	353	4	SAC 13	89	86	
7	1	373	4	SAC 13	100	85	
8	1	373	8	SAC 13	100	97	
9	2	333	4	NR 50	43		72
10	2	353	4	NR 50	62		77
11	2	373	4	NR 50	69		81
12	2	373	8	NR 50	54		94
13	2	333	4	SAC 13	61		78
14	2	353	4	SAC 13	85		86
15	2	373	4	SAC 13	99		85
16	2	373	8	SAC 13	100		98

Note. The anisole to acid chloride mass ratio is 4 and 8; the reaction time is 2 h.

TABLE 2

Acylation of Different Aromatic Compounds with 1, Selectivity >97%

					
yield [%]	NR 50	<1	10	26	59
	SAC 13	7	37	58	97

Note. Reaction conditions: 2.5 g **1**, 20 g aromatic compound, 0.5 g catalyst, $T = 373$ K; the reaction time is 2 h.

According to Eq. [2] in Scheme 1, the acylation products **4**, **5** can be transformed to the chlorinated derivatives **6** and **7**, respectively. This equilibrium reaction is shifted to the right-hand side by the irreversible hydrolysis of the chlorides by the produced water, according to Eq. [3] (Scheme 1). Both the chlorinated derivatives **6**, **7** and the free carboxylic acids **8**, **9** constitute the main byproducts during the acylation reaction.

By enhancing the reaction temperature, the solubility of the hydrogen chloride in the reaction solution is distinctly reduced; consequently the selectivity to the desired products **4**, **5** is enhanced. By increasing the amount of the aromatic component, the selectivity is raised even further, to values of 94 to 98%, according to runs 4, 8, 12, and 16 in Table 1. When using phenyl propionic acid chloride **5** as acylating agent, a ring closure reaction to form the 4-methoxy indanon **10** can take place according to Eq. [4] (Scheme 1). In the stoichiometric $AlCl_3$ catalyzed reaction this self-acylation makes up for the main side reaction, whereas in the heterogeneously catalyzed reaction it is detected only in traces, less than 1% selectivity.

The acylation of anisole over heterogeneous catalysts is often investigated due to the activated character of the aromatic compound refering to electrophilic substitution reactions. However, as a competitive alternative to highly active homogeneous catalysts, heterogeneous catalysts should have the potential to catalyze acylation reactions with lesser activated aromatic compounds. Therefore, we studied alternative aromatic compounds such as toluene and xylene in this reaction. Table 2 summarizes the results, which were obtained under the same reaction conditions as indicated in runs 4, 8, 12, and 16 (Table 1).

As the selectivity was very high in all runs (>97%), only the yields of the reaction are presented. With the Nafion/silica composite catalyst *m*-xylene and *o*-xylene are acylated in yields of 58 and 37%, respectively. In the acylation of toluene, however, only 7% of the desired product was achieved. However, it has to be taken into account that the reaction conditions are not optimized yet. The reaction time of two hours as well as the reaction temperature may be increased to ensure a higher conversion at a selectivity which is still on a high level. On the other hand, it is obvious that in contrast Nafion NR 50 shows a poorer catalytic performance.

In conclusion, the Nafion/silica composite material represents a promising tool for acid-catalyzed reactions. Entrapping nanosized Nafion particles in a silica-matrix effectively enhances the accessibility of the acid sites in comparison to the original material, Nafion NR 50. The acylation of anisole with carboxylic acid chlorides is performed very satisfactorily with short reaction times and very high selectivity. Even less active aromatic compounds such as *m*- and *o*-xylene are successfully acylated. It may be expected that because of their further optimization of the reaction conditions, Nafion/silica composite materials constitute competitive alternatives to traditional homogeneous catalysts.

ACKNOWLEDGMENTS

The authors are grateful to DuPont de Nemours & Company for financial support and for the permission to publish this work.

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