

PhD. Thesis

**THE SYNTHESIS AND APPLICATION OF ELECTROPHILIC
CATALYSTS FUNCTIONALIZED WITH SULFONIC ACID GROUPS**

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I. INTRODUCTION

It is estimated that catalyst-based manufacturing accounts for about 60% of chemicals production and 90% of processes. As a result, intensive research is being carried out in this field.

Organic transformations may be performed in the homogenous or heterogeneous phase. In homogenous reactions the distribution of the active sites is uniform and, consequently, molecules can collide without any difficulty. The reaction proceeds quickly with great efficiency and the rate-determining step is regulated by thermodynamics. The main disadvantage of homogenous catalytic reactions is that upon working up the reaction mixture the catalysts, in general, cannot be regenerated or reused. As a result, they accumulate as waste. Homogenous catalytic processes, therefore, are not very advantageous either from the economic or the environmental point of view.

The substitution of homogenous catalysts strongly motivates scientists. A possible solution is to fix the active sites on various solid supports so the chemical reaction takes place under heterogeneous conditions. Heterogeneous catalysts, compared to their homogenous counterparts, have several advantages. First, the separation of catalysts from the reaction mixture can easily be performed by simple filtration or decantation. Furthermore, heterogeneous catalysts can often be used under solvent-free conditions. The application of heterogeneous catalysts is particularly useful from the industrial point of view. They proceed with high efficiency, that is with high activity and selectivity. A further very important feature is that heterogeneous catalysts can be regenerated and reused for several catalytic cycles, which makes their application highly economical. In addition to these advantages, however, drawbacks have also to be mentioned. Namely, the distribution of active sites is not uniform and, therefore, some of the active site cannot be reached by the reactants. A further problem is the heterogeneous, that is, non-uniform strength of the active sites, and hindered diffusion is often encountered in heterogeneous systems.

Most of the catalytic reactions are electrophilic in nature. Depending on the acid strength of various catalysts they can be used in a wide variety of reactions. Electrophilic catalysts applied in homogenous reactions (HF, H₂SO₄, HNO₃, trifluoromethanesulfonic acid) have additional drawbacks. Due to the strong acidic character of these catalysts they are very corrosive and poisonous. The fast development of catalyst design, however, made it possible to apply various heterogeneous catalysts in industrially important electrophilic reactions. With

the use of heterogeneous acidic catalysts several environmental problems can be solved. Furthermore, technological applications can also be expanded using fluid and fixed-bed reactors. With the possibility of regeneration manufacturing can be even more economical.

In the Department of Organic Chemistry at the University of Szeged, electrophilic catalytic reactions have been extensively studied. Upon participating in this research project the subject of my dissertation was the synthesis and application of heterogeneous electrophilic catalysts in organic synthesis. The specific aim of these studies, based on literature information and our own previous results, was to synthesize sulfonic-acid functionalized solid electrophilic catalysts and apply these systems in various organic reactions.

We have investigated four catalytic systems. (i) Sulfonic-acid functionalized MCM-41, HMS and SBA-15 mesoporous systems were synthesized and a comparative study of their catalytic performance was made. (ii) The synthesis and catalytic performance of periodic mesoporous silica (PMO) systems were studied. (iii) The results acquired by studying Nafion H[®] systems having fluoroalkanesulfonic acid function, fit into the scope of the dissertation. In order to increase the specific surface area of Nafion H[®] resin, we prepared Nafion H[®]-silica catalysts by mechanochemical synthesis. The results were compared to those of SAC-13 a commercial Nafion H[®]-silica system with superacidic character. (iv) Finally, an ionic liquid with sulfonic acid groups as active sites was synthesized and examined. This was successfully entrapped into a silica matrix and thereby transformed into a heterogeneous acidic catalyst.

II. EXPERIMENTAL

Two synthesis methods were used to prepare MCM-41, HMS and SBA-15 type catalysts. A set of six catalysts was synthesized using co-condensation and another set was prepared by post-synthesis modification (grafting). We successfully synthesized MCM-41 catalysts with various pore sizes, where the external surface of the catalyst was covered with phenyl groups. These catalysts were used to carry out various shape-selective reactions. The fluoralkanesulfonic acid (Nafion) systems were manufactured by mechanochemical synthesis, whereas the sol-gel synthesis was applied to entrap the ionic liquid in a silica matrix.

The structure of the catalysts was examined by various instrumental techniques. These included X-ray diffraction (XRD), the analysis of adsorption-desorption isotherms (BET), diffuse infrared spectroscopy (DRIFT), Raman and X-ray photoelectrospectroscopy (XPS). The organic content of the catalysts was determined with a CHNS analyzer, whereas the amount of active sites was measured by acid-base titrations. Scanning electron microscopy (SEM and EDX) was also used to characterize fluoralkanesulfonic acid catalysts prepared by mechanochemistry.

The acid-catalyzed reactions in the liquid phase were carried out under atmospheric pressure in a round-bottom flask with the use of a reflux condenser and a magnetic stirrer. Samples withdrawn at certain time intervals were analyzed with a Hewlett Packard 5980 gas chromatograph equipped with a 50 m long HP1 column. The repeatability of the conversion was within ± 5 %. Products were identified by GC-MS (Hewlett Packard 5970 mass selective detector connected to a 5890 gas chromatograph) and ^1H NMR spectroscopy (Bruker DRX 500 NMR equipment).

III. NEW SCIENTIFIC RESULTS

A. MESOPOROUS CATALYSTS

1. MCM-41, HMS and SBA-15 type catalysts, synthesized with co-condensation and post synthetic modification, having propanesulfonic and benzenesulfonic acid groups as active sites were found to be very active in the butan-1-ol–acetic acid esterification reaction, and Friedel–Crafts alkylation of benzene and toluene with benzyl alcohol. The differences in reactivity could be correlated with the acid site density of the catalysts.
2. In the dimerization of 2-phenylpropene and the rearrangement-aromatization of 2,6,6-trimethylcyclohex-2-ene-1,4-dione catalysts with aromatic sulfonic acid groups with stronger acidic character were shown to exhibit higher activity.
3. The structural features of various types of mesoporous silicas (MCM-41, HMS and SBA-15) did not affect the catalytic activity and selectivity of the catalysts. That is, neither co-condensation nor post-synthesis modification was found to show any preferable catalytic performance. It may be concluded that various factors should be taken into account for a given reaction in order to decide, which method leads to a more active catalyst.

B. SHAPE SELECTIVE CATALYSTS

4. We synthesized MCM-41 structures with narrow (1,6 nm) pore size. First, the external wall of the MCM-41 was covered with phenyl groups then the sample was functionalized by grafting. The original hexagonal structure of the catalyst changed only slightly.
5. Four catalysts were tested in various reactions and it was concluded that by carefully tailoring the structure of the catalysts it is possible to synthesize mesoporous systems suitable for shape selective reactions provided reacting molecules with appropriate sizes are selected.
 - In the reaction of phenol with 2-methylpropan-2-ol the selectivity of monoalkylated products (*orto/para* ratio) changes significantly with narrow pore sizes and with blocked external wall structures.
 - In the ring opening of *mezo*-hydrobenzoin the transformation requiring the migration of phenyl groups having larger size becomes slower.

- In the acetal formation of aromatic methyl ketones an inverse relationship was established between molecular size and the rate of the reaction. In competitive reactions the presence of a smaller ketone was shown to hinder or even stop the transformation of the larger ketone.

C. PERIODIC MESOPOROUS MATERIALS

6. We successfully functionalized sulfonic-acid containing periodic mesoporous benzene-silica materials (PMO) where the benzene rings – being incorporated in the wall of the catalyst – was sulfonated with chlorosulfonic acid. The structure of the catalyst was similar to that previously reported.
7. The functionalized benzene-silica catalysts were active in the Friedel–Crafts alkylation of benzene and toluene. PMO functionalized with benzenesulfonic acid groups were found to be the most active. These results are similar to those observed for other mesoporous catalysts.
8. In the gas-phase reaction of phenol with propan-2-ol, PMO functionalized with propanesulfonic acid exhibited the highest specific activity and gave the monoalkylated products with the highest selectivity. This latter feature can be correlated with the smaller pore size.
9. We proved that PMO systems have greater hydrothermal stability and, therefore, they are more suitable for gas-phase reactions than the mesoporous catalytic systems (MCM-41, HMS and SBA-15) studied.
10. For functionalized benzene-silica systems the following observations were made.
 - a. Catalysts with the highest number of active sites were the most active in Fries-rearrangement. In addition, they give the *para*-substituted product in increased amounts, which is attributed to the smaller pore sizes.
 - b. Catalysts functionalized with benzenesulfonic acid groups having stronger acidic character showed higher activity in the dimerization of 2-phenylpropene and the rearrangement-aromatization of 2,6,6-trimethylcyclohex-2-ene-1,4-dione. In these cases products requiring the participation of stronger acidic sites were formed with high selectivity.

D. NAFION-SILICA CATALYSTS

11. In the mechanochemical synthesis of Nafion H[®]-silica catalysts prolonged milling was shown to result in a decrease in specific surface area. This is due to the fact that local high energy conditions bring about the aggregation of smaller particles.
12. The Nafion H[®]-silica catalysts synthesized by mechanochemistry were active in Friedel–Crafts alkylations. Optimal conditions for a catalyst with high activity were established: the use of a polystyrene mill, a Fluka-type silica gel, and medium milling time (15 h).
13. The same catalyst was the most active in the dimerization of 2-phenylpropene and its activity exceeded that of the commercially available solid acid Nafion SAC-13.

E. IONIC LIQUID, IONIC LIQUID ENTRAPPED IN SILICA

14. We successfully synthesized an imidazolium-based ionic liquid functionalized with butanesulfonic acid function, which was then incorporated into a silica matrix by the sol–gel method.
15. The ionic liquid was active and reusable in Friedel–Crafts alkylations and in the *ortho*-Claisen rearrangement.
16. The ionic liquid immobilized in silica was also very active and reusable in Friedel–Crafts alkylations and the tetrahydropyranylation of alcohols.

LIST OF PUBLICATIONS

Papers related to the subject of the Thesis:

1. SiO₂-supported dodecatungstophosphoric acid and Nafion-H prepared by ball-milling for catalytic application
B. Rác, G. Mulas, A. Csongrádi, K. Lóki, Á. Molnár
Appl. Catal. A., **2005**, 282, 255
2. A comparative study of solid sulfonic acid catalysts based on various ordered mesoporous silica materials
B. Rác, Á. Molnár, P. Forgó, M. Mohai, I. Bertóti
J. Mol. Catal. A: Chem., **2006**, 244, 46
3. Organic transformations over silica materials modified by covalently bonded surface functional groups
Á. Molnár, **B. Rác**
Current Organic Chemistry (in press.)
4. Sulfonic acid-functionalized phenylene-bridged periodic mesoporous organosilanes as catalyst materials
B. Rác, P. Hegyes, P. Forgó, Á. Molnár
Appl. Catal. A, **2006**, 299, 193
5. Shape selective application of sulfonic acid functionalized MCM-41 materials
B. Rác, M. Nagy, I. Pálinkó, Á. Molnár
Appl. Catal. A., (submitted)

Other publications:

1. M. Pisarek, M. Janik-Czachor, P. Kedzierzawski, Á. Molnár, **B. Rác**, A Szummer
Modification of catalytic Activity of Cu-Ti amorphous alloy ribbons by cathodic hydrogen charging
Polish J. Chem., **2004**, 78, 1379
2. M. Pisarek, M. Janik-Czachor, A. Gebert, Á. Molnár, P. Kedzierzawski **B. Rác**
Effect of cathodic hydrogen charging on catalytic activity of Cu-Hf amorphous alloys
Appl. Catal. A., **2004**, 267, 1
3. D. Méhn, Z. Kónya, J. Halász, J. B. Nagy, **B. Rác**, Á. Molnár and I. Kiricsi
Flexibility of the MCM-41 structure: pore expansion and wall-thickening in MCM-41 derivatives
Appl. Catal. A., **2002**, 232, 67

Lectures and posters related to the subject of the Thesis:

1. Á. Molnár, **B. Rác**, V. Matits, Á. Kukovecz, Z. Kónya, I. Kiricsi
Characterization of acidic solids prepared by postsynthetic modification or immobilization
14th Int. Symposium on Reactivity of Solids, Budapest, 2000
Program and Abstracts, p. 161
2. A. Papp, **B. Rác**, Á. Molnár
Organic transformations with functionalized solids
6th Pannonian Int. Symposium on Catalysis, Obergurgl, Austria, 2002
Book of Abstracts, P-44, p. 176.
3. **Rác Bulcsú**, Csongrádi Anikó, Molnár Árpád
Mechanokémiai szintézissel készült SiO₂ hordozós heterofoszforvolfrámsav katalizátorok vizsgálata
Vegyészkonferencia, Hajdúszoboszló, 2003
Program és előadásösszefoglalók, P-91, 139. old.
4. **B. Rác**, A. Csongrádi, Á. Molnár
The study of mechanochemically synthesized 12-tungstophosphoric acid catalysts
EUROPACAT VI, Innsbruck, 2003
Programme, A1.021.
5. **B. Rác**, G. Mulas, A. Csongrádi, K. Lóki, Á. Molnár
Mechanochemical synthesis of heteropoly acid/silica and Nafion/silica composite materials and their use as catalysts in electrophilic transformations
7th International Symposium on New Methods of Reactivity Modification of Amorphous and Nanocrystalline Materials, Warsaw, 2003
Programme, P1, 28. old.
6. **B. Rác**, M. Nagy, Á. Molnár
Synthesis and catalytic application of sulfonic acid functionalized MCM-41 with various pore sizes
7th Pannonian Int. Symposium on Catalysis, Srní (Czech Republic), 2004
Abstracts, p. 82.

Other lectures and posters:

7. M. Pisarek, M. Janik-Czachor, P. Kadzierzawski, A. Szummer, Á. Molnár, **B. Rác**, S.M. Filipek, P. Mack
Modification of catalytic activity of Cu-based amorphous alloys by hydrogen charging
7th International Symposium on New Methods of Reactivity Modification of Amorphous and Nanocrystalline Materials, Warsaw, 2003
Programme, 14. old.

8. M. Pisarek, M. Janik-Czachor, P. Kadzierzawski, A. Szummer, Á. Molnár, **B. Rác**, S.M. Filipek, P. Mack
Modification of catalytic activity of Cu-based amorphous alloys by hydrogen charging
7th International Symposium on New Methods of Reactivity Modification of Amorphous and Nanocrystalline Materials, Warsaw, 2003
Programme, 14. old.
9. M. Pisarek, M. Janik-Czachor, A. Gebert, Á. Molnár, P. Kadzierzawski, **B. Rác**
Modification of catalytic activity of Cu-based amorphous alloys by cathodic hydrogen charging
17th School on Physics and Chemistry of Solids, Bialowieza (Poland), 2005
Program & Abstracts, p. L16
10. M. Janik-Czachor, M. Pisarek, A. Molnar, **B. Rac**
Cathodic hydrogen charging as a tool to activate Cu-Ti amorphous alloy catalysts
208th ECS Meeting, Los Angeles, 2005
Meeting Program, 375, PS-73.
11. Á. Mastalír, B. Rác, Z. Király, Á. Molnár, I. Dékány
In situ generation of Pd nanoparticles in MCM-41
3rd Zsigmondy Colloquim, Berlin, Germany, 2005
Book of Abstracts, Talk 21, p.37.

LIST OF IMPACT FACTORS (i)

Papers related to the subject of the Thesis:

1. publication	i = 2,378
2. publication	i = 2,316
3. publication	i = 2,775
4. publication	i = 2,378
5. publication	i = 2,378

$$\Sigma i = 12,225$$

Other publications:

1. publication	i = 0,640
2. publication	i = 2,378
3. publication	i = 1,915

$$\Sigma i = 4,933$$

