High Surface Area Nafion[†] Resin/Silica Nanocomposites: A New Class of Solid Acid Catalyst

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Received December 14, 1995. Revised Manuscript Received June 8, 1996[⊗]

Abstract: Nafion resin, a perfluorinated ion-exchange polymer, has been used as a heterogeneous strong acid catalyst for a range of reactions; however, in nonpolar solvents or for gas phase reactions the activity is limited due to the extremely low surface area of the polymer beads (<0.02 m^2 g^{-1}). In this paper we describe a novel nanocomposite of Nafion resin, in which small (20−60 nm diameter) Nafion resin particles are entrapped within a porous silica network. This material combines the excellent solid acid catalyst properties of Nafion resin with the desirable porous support characteristics of silica. BET surface area is typically in the range of 150−500 m^2 g^{-1} for the composite. Assuming the Nafion resin particles are dense spheres we estimate the effective surface area of the Nafion resin alone to be in the range of 153 (20 nm spheres) to 50 (60 nm spheres) m^2 g^{-1}. This new material has been developed using an in situ sol−gel technique wherein solutions of Nafion resin are mixed with soluble silicon sources to form a gel, which is dried to a clear hard glass-like material. These new porous nanocomposites offer the potential for significantly enhanced activity due to the increased accessibility of the Nafion resin-based acid sites. We show examples of catalytic reactions in which the activity per unit weight of Nafion resin has been found to be at least 100 times higher in the composite than the pure polymer.

Introduction

There has been considerable interest recently, driven by environmental considerations and safety concerns, to find solid acid alternatives for very hazardous and corrosive mineral acid catalysts such as hydrofluoric and sulfuric acids[1,2] used in commercial chemical processes. Acidic ion-exchange polymer resins represent one class of potential solid acid materials. In particular, Nafion resin, a perfluorosulfonic acid resin, has been shown to be an effective catalyst for a wide range of acid-catalyzed reactions.[3−5]

Nafion resin has been described as a superacidic catalyst which in the acid form has a terminal -CF$_2$CF$_2$SO$_3$H group. Nafion resin is a copolymer of tetrafluoroethene and perfluoro-2-(fluorosulfonylethoxy)propyl vinyl ether. The general structure is shown below,

$$[(CF_2CF_2)_nCFCF_2]_x$$
$$(OCF_2CF)_mOCF_2CF_2SO_3H$$
$$CF_3$$
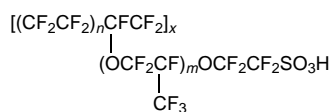
where $m = 1$, 2, or 3, and n typically has a value of about 6−7, with x about 1000. It has been suggested that the acid groups in Nafion resin have a Hammett acidity ($-H_o \sim 12$) similar to 100% sulfuric acid.[4] The high acid strength and chemical inertness of the fluorocarbon backbone make Nafion resin an attractive replacement for strong homogeneous acid catalysts. In fact, the use of Nafion resin for the catalysis of a variety of reactions including alkylations, acylations, isomerizations, esterifications, hydrations and dehydrations, nitrations, and etherifications has been described in detail by Olah et al.[3] Nafion

resin is available commercially in the form of millimeter sized beads known as Nafion NR50 resin. The surface area of the resin in this form is very low (typically 0.02 m^2 g^{-1} or less), and most of the active sites are buried within the polymer beads. Under many types of reaction conditions, these sites are inaccessible or poorly accessible, and as a result the observed activity for many reactions is very low.

In this paper we describe the formation and properties of a nanocomposite of nanometer sized Nafion resin particles entrapped within a highly porous silica network, which significantly improved the accessibility of the acid groups. The materials are prepared using a sol−gel technique. The ability to synthesize materials at low temperatures using the sol−gel reaction has led to a range of unique microstructures.[6−9] Examples include enzyme containing silicates for use in biosensors,[8] incorporation of organics designed for nonlinear optical applications and organically modified silicates.[9] In this work, we focus upon the use of the nanocomposite concept in the design of materials for catalysis. The composites that we have developed, due to their high surface area and readily accessible active sites, greatly expand the range of reaction conditions under which Nafion resin can be used. Gas phase reactions and also reactions using nonpolar reactants or solvents show orders of magnitude increase in reaction rate using the new materials. Furthermore, with fairly straightforward variations in synthesis conditions, we can tailor the microstructure; for example, the pore size can be varied in a controlled way.

There is an analogy between the nanocomposites that we have described here and the development several years ago of

† Nafion is a registered trademark of E. I. DuPont de Nemours & Co.
⊗ Abstract published in *Advance ACS Abstracts,* July 15, 1996.
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macroreticular polystyrene-based ion-exchange resins.[10,11] Sulfonated gel-type polystyrene materials displayed very slow diffusional behavior of reactants within their framework and low catalytic activity; however, a breakthrough in this area came in the early 1960s with the development of macroreticular resins. Macroreticular resins are organic polymer microstructures with high surface area, and well-defined pore structures, which allow ready access to a variety of molecules compared to the gel-based materials. These macroreticular resins are presently used in a number of industrial processes. For example, Amberlyst-15 resin is used in the manufacture of methyl tertiary butyl ether (MTBE), an octane enhancer for oxygenated fuels.[12]

Experimental Section

Starting Materials. Tetramethyl orthosilicate [$Si(MeO)_4$] and tetraethyl orthosilicate [$Si(EtO)_4$] were obtained from Fluka and were used as received. Sodium silicate solutions (29 wt % of silica) and Ludox colloidal silica (HSA 30) are available from DuPont (Wilmington, DE). $CaCO_3$ was obtained from Albafil (Adams, MA). The Nafion resin perfluorinated ion-exchange polymer used was in the form of a 5 wt % solution, which is prepared under pressure, in a mixed alcohol water system.[13] Solutions of this type have been used in a number of areas, for example, in the area of chemically modified electrodes[14] and in the preparation of polymer−electrolytic fuel cells.[15] The equivalent weight of the polymer is typically 1070. The Nafion resin solutions are available from Aldrich.

Typical Synthetic Conditions (13% by Weight of Nafion Resin in Silica). A typical procedure is as follows, although a number of variations will be described in the Results section to illustrate how the microstructure can be tailored with respect to pore size and surface area. A two step acid/base hydrolysis and condensation of the alkoxy silane was used in this synthesis (see Results section). A mixture of 204 g of $Si(MeO)_4$, 33 g of distilled water, and 3 g of 0.04 M HCl was stirred for 45 min to give a clear solution. To 300 mL of a Nafion resin solution (which contains 5 wt % of Nafion resin) was added 150 mL of a 0.4 M NaOH solution, while stirring. The NaOH solution was added over about 15 min. The silicon containing solution, prepared as described above, was added rapidly to the stirred Nafion resin/NaOH-containing solution. Within about 10−20 s, the solution gelled to form a hard solid mass, which was slightly opaque. The solid gel was placed in an oven (which was purged with a nitrogen gas flow to help remove the volatiles), and dried at about 95 °C, over a period of about 2 days, followed by drying under vacuum overnight (95 °C). The product was gently ground and passed through a 10-mesh screen. The resulting composite was reacidified by stirring with 500 mL of 3.5 M HCl, aqueous solution, and then washed with deionized water. This process was repeated four times. The material was then treated with 25 wt % nitric acid overnight at 75 °C followed by washing with deionized water. Finally, the product was dried under vacuum at 100 °C for 24 h, yielding a hard glass-like material with a weight of 98 g compared to a theoretical weight of 95 g (assuming complete conversion to SiO_2 (80 g) and the weight of Nafion resin added (15 g)).

The nanocomposite has also been prepared using other precursors including alkali metal silicates and colloidal silica. The general formation of those has been described in the literature for pure silica.[16−25]

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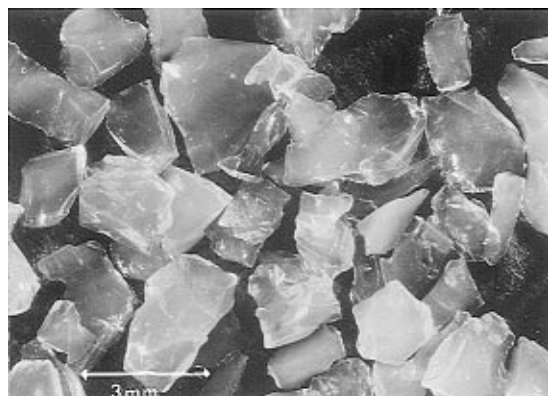(21) Mackenzie, J. D. *J. Non-Cryst. Sol.* **1988**, *100*, 162−168.

Characterization Methods and Catalysis Studies. Fourier transform infrared spectroscopy (FTIR) was carried out using a Nicolet Model 510 apparatus, using the KBr pellet technique. Nuclear magnetic resonance was performed in the solid state using a Chemagnetics CMX spectrophotometer (117.8 MHz). For the thermogravimetric studies, the apparatus used was a TGA V5.1 and a DTA VA.1C, both from DuPont. Elemental analysis was performed by Galbraith Laboratories. Microstructural analysis combined with energy dispersive X-ray analysis (EDX) was performed using a Hitachi S-5000SP scanning electron microscope and a Noran Voyager elemental analyzer, respectively. BET surface area, pore diameter, and BJH cumulative pore volume were obtained using a Micromeritics instrument.

Catalytic reactions were carried out using a batch reactor. Gas chromatography (GC) was obtained using an HP 1890 Series II GC, with an FID detector. In all catalysis experiments, the reactants and solvents were dried for at least 24 h over 4A molecular sieves, and the Nafion resin-based catalysts, including the pure Nafion NR50 resin, were dried at 150 °C under vacuum overnight. All of the reactions were performed under an atmosphere of nitrogen, and the glassware was dried just prior to use.

Results

A new composite of Nafion resin dispersed at the nanometer level within a porous high surface area silica has been developed using an in situ sol−gel technique.

The formation of silica networks, using sol−gel chemistry, is reasonably well understood, and the details have been described in a number of publications for silica.[16−25] The generic chemical processing using tetramethylorthosilicate as a silica source can be described as follows.

$$Si(OCH_3)_4 + 4H_2O \xrightarrow{H^+/OH^-} Si(OH)_4 + 4CH_3OH$$

$$nSi(OH)_4 \rightarrow nSiO_2 + (2n)H_2O$$
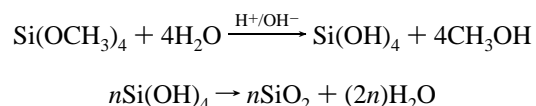
The procedure which we have employed in forming the Nafion resin/silica composites is similar to the so-called two step, acid/base, hydrolysis and condensation, which has been described in detail for pure silica.[24,25] The two step refers to first prehydrolyzing the silicon alkoxides, followed by a second base treatment step, which accelerates the condensation leading to gelation. In the procedure outlined, when the the soluble silicon-containing solution is added to the Nafion resin solution (which contains NaOH to control the silica gelation), the whole system gels within a few seconds. The gelation rate can be controlled by altering the pH and also the concentration of the silica. The hard gel is then dried to remove the solvent. The final dried glass-like composites are clear to slightly opaque (Figure 1). The materials are highly porous, with a surface area (determined by BET for the 13 wt % composite), pore volume, and pore diameter determined to be 344 m^2 g^{-1}, 0.85 cm^3 g^{-1}, and 9.8 nm, respectively (Table 1). Compared to Nafion NR50 resin, which has a surface area of about 0.02 m^2 g^{-1}, an increase in several orders of magnitude is found. The surface area for the composite is of course the additive value for both the silica and the Nafion resin.

One attractive feature of the sol−gel process is that the microstructure can be controlled by varying the processing conditions. We have found, for example, that we can readily tailor the pore diameter (and surface area) by controlling the pH. By carrying out the synthesis with a higher base concentra-

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Figure 1. Optical micrograph of sol−gel derived Nafion resin/silica nanocomposite.

Table 1. Effect of pH on the Surface Area, Pore Volume, and Pore Size of Nafion Resin/Silica Composites

acid/base	surface area, $m^2 \ g^{-1}$	pore diam, nm	pore vol, $cm^3 \ g^{-1}$
0.01 M HCl	563	2.1	0.15
0.08 M NaOH	344	9.8	0.85
0.16 M NaOH	154	20	0.84
0.24 M NaOH	85	25	0.75

tion (for example, using 0.8 M NaOH instead of 0.4 M NaOH as described in the Experimental Section), pore diameters in the range of 20 nm are obtained. The use of higher base concentrations is known to result in larger pore diameters within silica-based systems.[16,17] In addition, we have found that gels prepared using acid only catalyzed reactions (typically setting the acid concentration to 0.01 M HCl in the synthesis) lead to finer pore diameters in the range of about 2 nm. In this latter case, the gelation rate is very slow. The silica and Nafion resin containing solution are heated at 65 °C in a sealed vessel overnight, after which point gelation occurred. Table 1 shows a series of materials which we have prepared with different pore characteristics, by varying the pH. The pore size can be varied from 2 to 25 nm.

Dual porosity gels have also been prepared using modifications of the procedure as described in the Experimental Section. In this case, 150 g of $CaCO_3$ is added to the Nafion resin solution (containing the NaOH). Following gelation, the $CaCO_3$ particles also become entrapped. Acid treatment of the dried gel dissolves out these particles, generating calcium chloride and CO_2. This in turn introduces large, approximately 500 nm sized pores within the microstructure. Figure 2 is a scanning electron micrograph (SEM) of a dual porosity material, which shows both small (about 10 nm) and large (about 500 nm) pores. The ability to develop structures of interconnected small and large pores may be important in designing solid acid catalysts for large molecule, oligomeric or polymeric formation/ transformations. The average diameter of the smaller pores (2− 25 nm) and the larger pores (ca. 500 nm) can be readily altered by adjusting the pH of gelation and the particle size of the $CaCO_3$, respectively.

The type of silicate precursor does not appear to be critical in the synthesis of these composites. Materials have been synthesized using a variety of silicon sources. Tetraethyl orthosilicate, $Si(EtO)_4$, can be partially hydrolyzed and condensed (for each 1 mol of $Si(EtO)_4$, 3.2 mol of water and an acid catalyst, 10^{-2} mol of HCl, was added); however, the initial hydrolysis is slower and takes about 3 h to complete. $Si(MeO)_4$ is hydrolyzed in a few minutes. Gelation, drying, and reacidification are carried out in the same way. Typical surface area
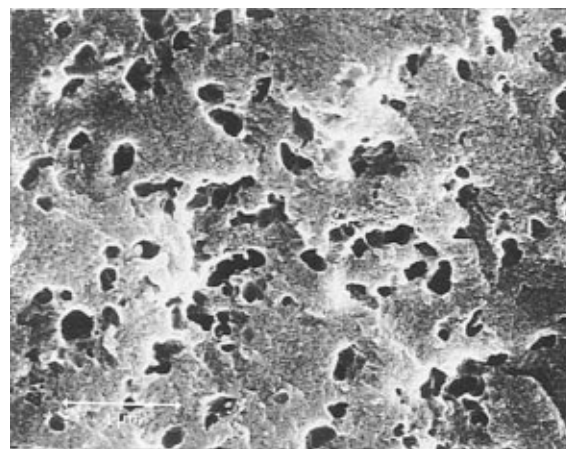

Figure 2. Scanning electron micrograph of a Nafion resin/silica nanocomposite with dual porosity.

data on a composite containing about 10 wt % of Nafion resin made via $Si(EtO)_4$ had values of surface area, pore volume, and pore diameter of 330 $m^2 \ g^{-1}$, 0.75 $cm^3 \ g^{-1}$, and 7.5 nm, respectively. Similar to expectations from Table 1, composites have also been made using sodium silicate solutions or Ludox HS30 as the silicon source. In these latter cases, the Nafion resin solution is first added to the silicon source and the pH adjusted to about 6−7 to induce gelation. Using sodium silicate, sodium silicate solution (700 mL containing about 9 wt % of silica) was added slowly to 100 g of a 5 wt % Nafion resin containing solution. The pH was adjusted to 7, after which point the solution formed a gel. Upon drying and reacidification, the dry glass-like composite had a surface area, pore volume, and pore diameter of 387 $m^2 \ g^{-1}$, 0.81 $cm^3 \ g^{-1}$, and 7.1 nm, respectively. This latter approach is one of the commonly used methods to make silica gels based upon mixing an acid with a solution of "water glass", which consists of orthosilicates (Na_4SiO_4), metasilicates (Na_2SiO_3), and related compounds (see page 117, ref 17).

The Nafion resin loading can also be varied within the composite. By varying the ratio of the Nafion resin concentration to the concentration of the $Si(OMe)_4$ (in the case of the alkoxide route), composites have been prepared containing 8, 10, 13, 25, 40, 60, and 80 wt % of Nafion resin. Using the same base concentration as described in the Experimental Section, the surface area remains very high, up to at least 40 wt % of Nafion resin within the composite. At higher loadings (60 and 80 wt %) the surface area begins to drop off quite dramatically. Values for a number of the composites (surface area $m^2 \ g^{-1}$, pore volume $cm^3 \ g^{-1}$, and pore diameter nm) are as follows: 8 wt % (412, 0.84, and 10.3), 10 wt % (270, 0.59, and 6.5), 40 wt % (468, 1.05, and 8.9), and 60 wt % (34, 0.15, and 15). Presumably at the higher polymer loading the polymer microstructure starts to dominate the pore characteristics disrupting the continuity of the porous silica network.

Discussion

The microstructural data indicate that these high surface area materials can be most accurately described as nanocomposites. The Nafion resin is highly dispersed within and throughout the porous silica network, on the tens of nanometers level. The microstructure may be regarded as a porous silica network which contains "pockets" of very strong acid sites, the Nafion resin polymer, in domains of about 20−60 nm. These sites appear to be readily accessible to reactants via the interconnected porous channels.
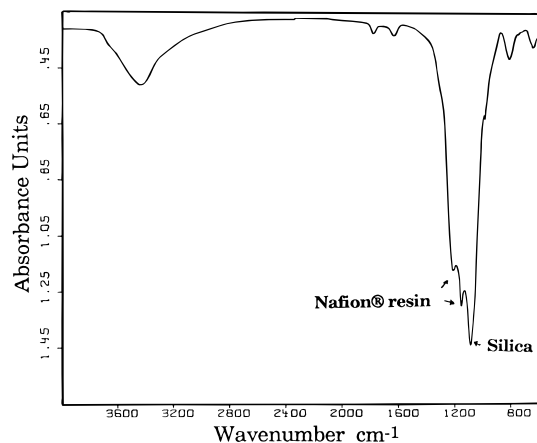
Figure 3. FTIR of a Nafion resin/silica nanocomposite.

Figure 4. SEM of a 40 wt % Nafion resin/silica composite.

Figure 5. TEM of a 13 wt % Nafion resin/silica composite.

Physical Characterization of Materials. FTIR spectra of the composite can be interpreted as a linear combination of the individual silica and Nafion resin spectra. Figure 3 shows the FTIR spectrum of a composite which contains about 40 wt % of Nafion resin. The main peak positions (cm^{-1}) are found at 630, 800 (s), 1080 (s), 1160 (s), 1210 (s), 1640, 1780, and 3450 (b). These correspond to the additive peak positions found in the resin and silica. For example, Nafion resin has strong bands at 1210 and 1160 cm^{-1} which correspond to the C$-$F stretching modes. The peaks at 1080 cm^{-1} correspond to the Si$-$O$-$Si stretching vibration, and the broad band near 3450 cm^{-1} corresponds to the structural hydroxyl groups, and physisorbed water typical of silica gels.

The presence of the Nafion resin domains is also implied by solid state ^{19}F NMR. In the composite, peak positions at -82.2, -123.6 (strong band with a small shoulder), -141, and -146 ppm are obtained (spectrum not shown). The pure Nafion resin itself has peaks at -81.9, -123.3, -141, and -144.7 in good agreement with the above. These bands are made up of contributions from up to three different F atoms within the polymer structure. In the sulfonyl fluoride form of Nafion ($-SO_2F$), the precursor to the sulfonic acid, the broad band at -123.3 ppm, can be resolved into three bands at -116, -112, and -120 ppm. The peaks at -116^* and $-120°$ ppm correspond to fluorines in the polymer backbone ($-CF_2°CF_2^*CF-(OR_f)CF_2-$).

The presence of Brönsted acid sites was confirmed by absorbing pyridine on to the acid sites. The excess pyridine was removed by extensive washing with distilled water. The presence of the pyridinium ion was demonstrated by FTIR (peaks at both 1542 and 1491 cm^{-1}).[26]

Thermogravimetric analysis (TGA) is useful in verifying both the presence and the amount of Nafion resin within the composites. The TGA of a porous silica (prepared in the absence of the Nafion resin) shows less than 5% weight loss on heating at 10 °C/min, from room temperature up to about 800 °C. This low weight loss is due to residual moisture (<200 °C), and at higher temperatures, surface silanols are lost to form siloxane bonds on the surface (Si$-$O$-$Si). In contrast, the composite shows a dramatic weight loss which starts around 400 °C and is complete at about 500 °C. This event occurs at exactly the same temperature as found for the decomposition and volatilization of the polymer alone. The inherent thermal stability of the entrapped Nafion resin is about the same as Nafion NR50 resin which begins to lose the sulfonate groups
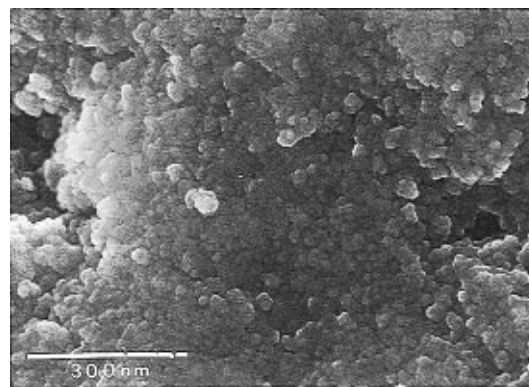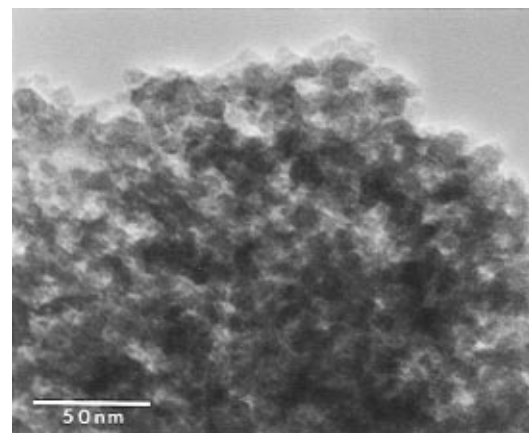
at about 280 °C.[27] These temperature stabilities are of course much higher than hydrocarbon-based sulfonate ion-exchanged resins, such as Amberlyst-15, which is stable only up to 130 °C.

For the composite, weight loss over the 400$-$500 °C temperature range can be used to estimate the loading of the Nafion resin. We have found very good agreement between Nafion resin concentration measured from the TGA and the theoretical values. Synthesis aimed at 40 and 13 wt % Nafion resin/silica showed a weight loss in the perfluorocarbon region (400$-$500 °C) of 39 and 12.8 wt %, respectively. Elemental analysis was also in reasonable agreement with the expected values. Values for the 13 wt % Nafion resin in silica were as follows: Si (37.5 found, 38.7 calcd), S (0.39 found, 0.35 calcd) and F (7.4 found, 8.9 calcd).

The microstructure has been investigated using SEM, TEM, and small angle X-ray scattering (SAXS). Figure 4 is an SEM of the surface of a composite which contains about 40 wt % Nafion resin (prepared under basic conditions). The microstructure is particulate in nature, with primary particles in the range of 5$-$15 nm. During the hydrolysis and condensation of the silica network, this kind of particulate growth is common using base catalyzed reactions.[16] Gelation occurs following nucleation and growth of the primary particles, via particle condensation and cross-linking, to form the extended network. SAXS analysis is also consistent with domains in the range of about 8 nm. Close examination of the microstructure reveals regions of porosity. Figure 5, is a TEM of the composite, again showing the particulate substructure and also the porosity. The measured pore diameter (from nitrogen adsorption isotherms) is about 10 nm.

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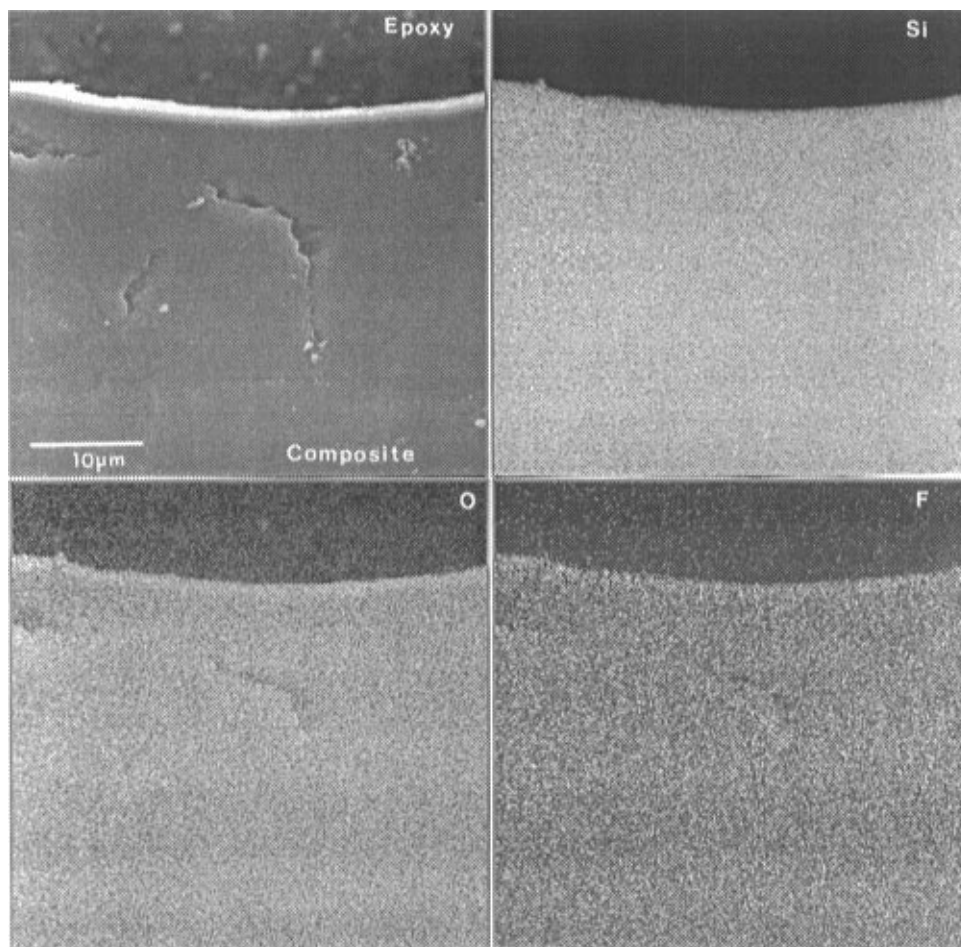
Figure 6. EDX, elemental mapping of a 13 wt % Nafion resin/silica composite, showing a uniform Si, F, and O distribution.

Energy dispersive X-ray analysis (EDX) of the composite shows the Nafion resin and the silica are intimately mixed at the nanometer level. Both as prepared and also polished cross sections were investigated using EDX. Two different beam cross sections were employed, spot mode (which analyzes a small <100 nm area, in this case for F and Si) and a broad-area beam, several micrometers in size. Chunks of material (a few millimeters in size) were mounted in epoxy resin, and the particles were polished to give a flat, smooth cross section. This reveals the interior of the composite material. Analysis showed the presence of Si, F, O, and C, all of which were present across the whole interior of the particle up to the edge. Several areas within the Nafion resin/silica gel particle and several different gel particles were analyzed. In all cases within the beam resolution, ~100 nm, wherever Si was detected, F was also detected showing the intimate mixture of the two. No area enriched entirely in Si or entirely F was observed. The 13% Nafion resin composite was analyzed using elemental dot mapping (10 nm pore diameter composites). A uniform distribution of the Nafion resin within the silica is found, with the same C, Si, O, and F ratio across the whole particle (Figure 6).

We also examined the surface area, pore size, pore size distribution, and SEM of composites calcined to 600 °C, at which temperature the polymer is completely removed. The data are consistent with the Nafion resin being distributed on a scale of 60 nm (or less). Nitrogen adsorption isotherms indicated that a new population of pores not present in the starting material with a pore size distribution in the 20−60 nm range was present, with a peak around 30 nm. This indicates the Nafion resin may be dispersed within the silica in clusters typically about 30 nm. This is also in agreement with
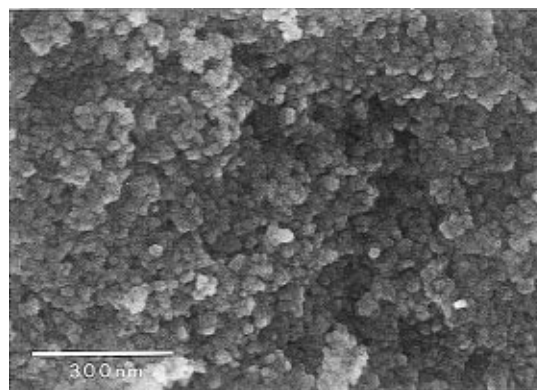

Figure 7. SEM of composite heated to 600 °C to remove the polymer.

measurement of the original polymer solution using quasi-elastic light scattering data. Measurements using quasi-elastic light scattering from the Nafion resin solution showed a large proportion of the polymer was present as particles with a typical hydrodynamic diameter of about 50−70 nm and thus may be regarded more as a colloidal solution rather than a true solution. We note, however, that the presence of smaller particles cannot be ruled out, since the scattering pattern would be dominated by the larger particles. Figure 7, is an SEM of the calcined material. The presence of voids with diameters in the range 20−60 nm is apparent (as compared to Figure 4), which is consistent with both the light scattering data and the pore size distribution (following calcination). These results may imply that the particle size of the Nafion resin is approximately maintained throughout the processing steps. Larger voids (>60 nm) were not observed. At 600 °C the silicate matrix undergoes
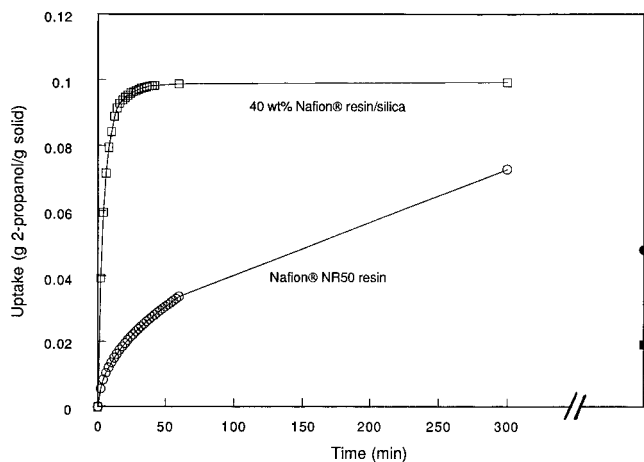
Figure 8. 2-Propanol mass changes on Nafion NR50 resin and the Nafion resin/silica composite. Data points at the right show the residual mass of absorbate after pumping the system back to 10^{-8} torr (25 °C).

very little microstructural change (except loss of silanols), and it is reasonable to assume the created voids in the composite reflect the original dispersion of the Nafion resin. Assuming the Nafion resin is 20−60 nm in size and if we also assume the particles are dense spheres, we estimate the effective surface area of the Nafion resin alone, within the 13 wt % composite, to be in the range of 153 (20 nm) to 50 (60 nm) $m^2\ g^{-1}$; however, we note the close proximity of the silica may reduce this value. A more detailed microscopy study is in progress.

We have also found that at higher Nafion resin loadings (40 wt %) and with larger pore diameters (20 nm) composites can be obtained in which the Nafion resin concentration increases slowly from the center to the outer edge. Under these conditions (with larger pore channels during drying), it seems likely that the polymer has some mobility in the initially formed gel. The Nafion resin polymer is locked into the structure at some point during the drying stage. For the 40 wt % composite, the center of the particles contains about 30 wt % of Nafion resin (from EDX) to about 50 wt % toward the outer edge. In all cases, however, both F and Si are intimately mixed on the nanometer level. The concept of designing in gradients is being investigated further.

Temperature Programmed Desorption and Catalytic Studies. These tailor-made catalysts show exceptional activity for a number of solid acid catalyzed reactions. In nonswelling solvents/reactants, where a lack of swelling may limit the numbers of accessible sites of Nafion NR50 resin, these new porous materials show very high reactivity. Much of the data we present can be rationalized based upon increasing the number of accessible acid sites through increasing the effective surface area of the Nafion resin within the composite microstructure.

Adsorption/Temperature Programmed Desorption. Several important contrasts between the reactivity of the composite and pure Nafion NR50 resin pellets can be illustrated using adsorption/temperature programmed desorption experiments. In these experiments, approximately 10 mg of catalyst is loaded into a vacuum microbalance. The sample is evacuated to background pressures of 10^{-8} torr and heated to 200 °C to remove water. After cooling to 25 °C, the sample is exposed to 10 torr of 2-propanol vapor. Weight changes are followed as the adsorption of 2-propanol onto the catalyst occurs. Data comparing a 40 wt % Nafion resin/silica composite to Nafion NR50 resin is shown in Figure 8. Uptake of 2-propanol into the composite is very rapid, and adsorption is complete within about 30 min. However, in the pure polymer, uptake is very slow and is not complete even after several hours. After 5 h of
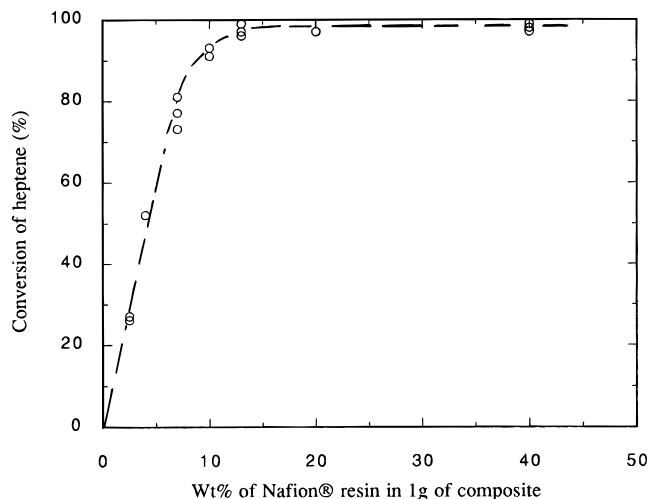

Figure 9. Conversion of heptene in the alkylation of toluene as a function of Nafion resin loading; 1 g of catalyst, 8.4 g of heptene, 15.6 g of toluene, reaction time 2 h at 100 °C.

2-propanol exposure, the system is re-evacuated. In both cases, after pumping the system back to 10^{-8} torr, a residual mass of adsorbate remains strongly bound to the catalyst. This residual mass is shown as the points at long times in Figure 8. For Nafion NR50 resin, the concentration of strongly bound 2-propanol (0.048 g/g) is equal to the measured proton content of the resin (0.8 mequiv/g). In the case of the composite, the strongly bound alcohol concentration (0.019 g/g) corresponds to about 75% of the total available acid site concentration (0.32 mequiv/g). The decrease from 0.1 to 0.019 g/g reflects the loss of weakly adsorbed 2-propanol molecules which fill the available pore volume within the composite. Similar results are found for silica alone (large initial 2-propanol uptake); however, upon evacuation, all of the 2-propanol is removed. The residual binding is due to attachment to the acid sites which in the case of the Nafion resin takes at least 2−3 h during the uptake stage (taken as the time to reach about 0.048 g/g, for the Nafion resin, Figure 8).

These results clearly show the enhanced accessibility of the acid sites in the composite structure. While it is possible for 2-propanol vapor to access all of the acid sites in Nafion NR50 resin by diffusion into the resin, it is a slow process. The resin has not come to equilibrium with the vapor during the 5 h of exposure represented in Figure 8. In contrast, the composite has equilibrated in minutes. Diffusion through the porous silica occurs readily, and even assuming the diffusion coefficient within the 20−60 nm Nafion resin domains is the same as in the polymer beads, diffusion over these short distances is rapid (few nm vs mm). Furthermore, this accessibility is enhanced in the composite without significantly reducing the number of acid sites per unit mass of resin. Less than 25% of the resin acid sites appear to be inaccessible to the reagent gas. We believe that this improved access to acid sites is the basis for the catalytic activity enhancements that we have observed using the composite.

In the final step of the adsorption/temperature programmed desorption experiment the 2-propanol-loaded catalyst is heated to 200 °C in vacuum. The sample weight falls as the adsorbed material is evolved. The partial pressures of evolved gases above the sample are followed by mass spectroscopy. Desorption from the composite is complete at 160 °C. Desorption from Nafion NR50 resin continues throughout the ramp and a subsequent hold at 200 °C for 1 h. In the first case, the products are exclusively propene and water. However, in the case of Nafion NR50 resin, in addition to water and propene, additional

hydrocarbon products are observed which are likely the result of secondary oligomerization and cracking reactions of propene. Dehydration chemistry is characteristic of the reactivity of 2-propanol on solid Brönsted acids.[28] The temperature over which it occurs on the Nafion resin/silica composite is similar to what is observed for the same reaction on the strong zeolitic solid acid, H-ZSM-5. This illustrates that the 2-propanol molecules are bound at strong acid sites and that the porous microstructure of the composite catalyst can improve not only the reagent access to those sites but, in cases where secondary reactions are a problem, the selectivity of Nafion resin as a solid acid.

α-Methylstyrene Dimerization. The dimerization of α-methylstyrene (AMS) was investigated with the Nafion resin/silica nanocomposite (containing 13 wt % Nafion resin with a pore size of about 10 nm) and Nafion NR50 resin. This reaction has been studied by Chaudhuri and Sharma[29] using a number of ion-exchange resins, clays, and Nafion NR50 resin as catalysts. The unsaturated dimers of AMS, particularly 2,4-diphenyl-4-methyl-1-pentene, are industrially important and are useful as chain-transfer agents or molecular weight regulators in the production of polymers. The reaction was carried out in a two neck flask, using 5 g of AMS stirred with 45 g of cumene as solvent (using the same conditions as used previously[29]). The catalyst loading was 0.5 g. The conversion was measured using GC analysis as a function of time. The rate of AMS dimerization in cumene was very slow using Nafion NR50 resin, with a conversion of <2% over 24 h. The corresponding rate constant was determined to be 0.14/(gcatal·h) (at 50 °C). The composite showed much higher activity, with ~100% conversion, over about 15 min (noting also that the Nafion resin content in the composite is only about 0.065 g compared to the Nafion NR50 resin, 0.5 g). For the composite the corresponding rate constant was determined to be 18.5/(gcatal·h) (at 50 °C). A control experiment using a pure silica gel prepared by the same procedure as the composite catalyst but without Nafion resin shows no AMS conversion after an hour under the same reaction conditions. It should be emphasized that in these experiments the same total weight of catalyst was used and therefore the activity on a Nafion resin basis within the composite is much more pronounced. Expressing the rate in terms of the total number of acid sites, values for the Nafion NR50 resin and the composite of 0.16 and 132.2 are obtained, respectively (/meqH$^+$·h). In this example, almost 3 orders of rate enhancement is observed, with the composite catalyst.

A more detailed kinetic study of this reaction using a range of catalysts and two types of solvents will be published separately.[30] For Nafion NR50 resin and Amberlyst-15 catalyzed AMS dimerization, the rate constants that we observed are consistent with those reported by Chaudhuri and Sharma.[29] We estimate that the fraction of sulfonic acid residues on the catalyst surface of NR50 is 0.004% (~4 × 10^{-5}), the so-called noninteraction accessibility suggested by Buttersack et al.[31] In the composite, where the Nafion resin now is dispersed into much smaller domains, we estimate that about 8−16% of the acid sites are accessible at the surface.

Friedel−Crafts Alkylations. The following alkylation reactions were investigated: toluene alkylation with heptene, diphenyl ether alkylation with dodecene, and propylation of

Table 2. The Rate Constant for Benzene Propylation to Cumene, Catalyzed by Solid Acid Catalysts in the Liquid Phase under Ambient Pressure (60 °C)

catalyst	13% Nafion resin/SiO$_2$	NR50	Amberlyst-15
rate (mM (gcat·h))	1.98	0.30	0.61
rate (mM/(meqH$^+$·h))	16.50	0.34	0.14
acid capacity (meqH$^+$/g)	0.12	0.89	4.4

benzene to form cumene. In these reactions, where the nonpolar reactants do not swell Nafion resin, very large rate enhancements are once again observed using composite catalysts. For example, the Friedel−Crafts alkylation reaction of toluene and 1-heptene was studied by adding 1 g of dried catalyst to a stirred solution of heptene (8.4 g) and toluene (15.6 g), at 100 °C (reaction time, 2 h). The procedure is similar to that reported previously where a number of alkylation reactions were investigated.[32] The sample was analyzed by gas chromatography (using dodecane as the standard), and the total heptene conversion was determined. A typical experiment, using 1 g of the 13 wt % nanocomposite materials, led to conversions of heptene at least 98%, i.e., almost complete conversion. If, however, the equivalent weight of Nafion NR50 resin is used (0.13 g), the conversion of heptene was less than 1% under the same reaction conditions. Again, the control experiment with pure silica gel shows no conversion under the same reaction conditions. Thus the actual conversion is about 100 times greater for the composite than the pure polymer. Figure 8 shows the conversion of heptene as a function of Nafion resin loading; 1 g of total catalyst was used. Composites containing about 10−40 wt % Nafion resin showed very high conversions, in the range of 90−100%. The conversion begins to drop off at the lower Nafion resin loadings, as expected.

Similar results were observed in the reaction of dodecene with diphenyl ether. Typical conditions involved addition of dodecene (8.4 g) to diphenyl ether (17 g) at 150 °C for 2 h. The conversion of dodecene was greater than 99% using 1 g of the 13% composite. As a comparison, using 0.13 g of Nafion NR50 resin, the conversion was about 5% for the same conditions.

Benzene Propylation. Benzene propylation to cumene was investigated with the 13% Nafion resin/silica composite, commercial Nafion NR50 resin, and Amberlyst-15 solid acid catalysts. The alkylation reaction was carried out in the liquid phase under ambient pressure and 60 °C by bubbling propylene through the bulk benzene solution containing a solid acid catalyst (2 g of catalyst). The benzene solution was presaturated with propylene at the reaction temperature, and then the catalyst was added. Aliquots were taken and analyzed by gas chromatography. In the case of Nafion NR50 resin, this gel-type of catalyst was pretreated in a pure benzene solution (benzene was found to swell the resin slightly) at 60 °C for 4 h to allow benzene to swell the catalyst completely before the reaction with propylene. A volume increase of about 7% was observed. Over all three catalysts, linear benzene conversion versus reaction time was observed. The rates of cumene formation over the solid catalysts were measured and are listed in Table 2. Highest activity was realized with the 13% Nafion resin/silica composite catalyst, which in this case is about 50 times more active than the Nafion NR50 resin catalyst under same conditions (on a meqH$^+$ basis). Notice that Amberlyst-15 with much higher acid capacity is also less active than the 13% Nafion resin/silica composite. This may be due to the fact that the intrinsic acid

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strength of Amberlyst-15 is weaker than that of Nafion as suggested by Olah and others.[3,5]

The rates of cumene formation from benzene propylation over the Amberlyst-15 and Nafion NR50 resin catalysts are consistent with literature values. Wesley and Gates[33] have reported a rate of 0.054 mM/(meqH$^+$·h) vs 0.14 mM/(meqH$^+$·h) in Table 2 for Amberlyst-15 under similar reaction conditions (55 °C versus the 60 °C employed here.) In that paper, they also show significantly higher activity from the macroporous resin Amberlyst-15 than the gel-form resin Dowex 50W-X2, -X4, and -X12 (Bio-Rad Laboratories). Klein and Widdecke[34] reported rates of 7.9 mM/(meqH$^+$·h) for Nafion resin and 2.8 mM/(meqH$^+$·h) for Amberlyst-15 at 75 °C. No further details of the experiment were described. They have developed a method for the fluorination of Amberlyst-15 type of polystyrene sulfonic acid resin with elemental fluorine in an attempt to increase the thermal stability and the acid strength of the resin. Indeed, the rate of cumene formation of 22.9 mM/(meqH$^+$·h) was reported for the fluorinated polystyrene sulfonic acid resin, which is about 3 times more active than the Nafion NR50 resin. Recently, a US patent issued to Allied-Signal Inc.[35] reported a similar approach with different preparation method for the fluorination of sulfonated polystyrene catalyst, and increased activity was realized as well. In comparison, we have seen more than 40 times higher activity from the 13 wt % Nafion resin/silica composite.

Nitration and Acylation. Most of the reactions described above involve reactants and solvents that do not swell the Nafion resin appreciably. We have also compared the reactivity of the composites with the pure Nafion resin in solvent or reactant systems that cause some swelling of the Nafion resin. Both an acylation and a nitration reaction have been studied. The utility of the composite under these aggressive reaction conditions also demonstrates the excellent chemical stability of the composites. The swelling has the effect of making the interior of the Nafion resin more accessible, and higher reaction rates would therefore be expected. In general, polar molecules such as water swell the Nafion resin. However, polar molecules also tend to adsorb on the Brönsted acid sites and can compete with reactants for acidic protons. In our experiments, we found that even in partially swelling systems the composites were in general more reactive although the difference is less pronounced.

The nitration of benzene using nitric acid was investigated using 75 g of benzene, 10 g of MgSO$_4$ (as a desiccant), 5 g of 1,3,5-trichlorobenzene (internal catalyst), and either 7.5 g of the 13 wt % Nafion resin in silica composite or 7.5 g of Nafion

NR50 resin. Nitric acid (90%) was fed into the reactor (under reflux) at a rate of about 0.06 mL/min. The reaction was maintained at reflux, and samples were removed at 15−30 min intervals for GC analysis. The average nitric acid conversion (and nitrobenzene selectivity), over the 150 min run time, was for the composite and Nafion NR50 resin, 82% (99.6%) and 64% (98.8%), respectively. In this example, a higher conversion was obtained using the composite, which of course contains only about one-eighth the amount of total Nafion resin. The acylation of *m*-xylene and benzoyl chloride was also studied, at a reaction temperature of 150 °C, where the Nafion resin swells by about 20 vol %. In this swelling system the conversion of benzoyl chloride using the composite was about 4 times that of the Nafion resin. In a typical experiment, 10.6 g of *m*-xylene was reacted with 7 g of benzoyl chloride, at 150 °C, with either 0.1 g of the Nafion NR 50 resin or about 0.8 g of the 13 wt % composite (i.e., the same amount of Nafion). Based upon GC analysis, the conversion of the benzoyl chloride to the acylated product was 17% (NR50) and 60% (composite), respectively.

Conclusions

We have developed a new high surface area Nafion resin/silica nanocomposite. The microstructure of this material can be described as an interconnected porous silica network into which the Nafion resin has been dispersed as 20−60 nm particulates. This new nanocomposite material has been shown to give excellent catalytic activity for a range of important industrial reactions. Activity enhancements of 10^2−10^3 (per unit weight of Nafion resin) relative to the pure polymer have been observed for a number of test reactions. We believe that the increased effective surface area and the ease of accessibility to the catalytically active sites in the composite have broadened considerably the utility of Nafion resin as a strong solid acid catalyst. The potential of Nafion resin as a replacement for strong mineral acids has been well documented in the work of Olah and others.[3] In composite form, the thermal stability and strong acidity can now be delivered more efficiently and over a wider range of reaction conditions.

JA9541950

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