

Dimerization of α -Methylstyrene (AMS) Catalyzed by Sulfonic Acid Resins: A Quantitative Kinetic Study

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The dimerization of α -methylstyrene was examined at 50°C and 1 atm in nonpolar cumene and polar *p*-cresol solvents, using both soluble liquid acids and resin-based solid acids as catalysts. In particular, the activities of a representative macroporous sulfonic acid resin, Amberlyst-15[®], and Nafion[®] perfluorosulfonic acid resin in three different microstructures, gel-type Nafion[®] NR-50 resin, a carbon-supported Nafion[®] resin, and a Nafion[®] resin/silica composite material, have been compared. The Nafion[®] resin/silica composites showed, by far, the highest activity. Supported Nafion[®] resin on carbon and Amberlyst-15[®] are effective catalysts as well and are all more active than pure Nafion[®] resin based on catalyst weight. None of the small molecule acids were sufficiently soluble to show significant catalytic action in the nonpolar solvent cumene. On the other hand, in the polar *p*-cresol media, the homogeneous acids showed relative activities in the same order as their pK_a s; and the strongest aqueous acid, triflic acid was more active than any of the resin catalysts on an acid equivalent basis. Among the resin catalysts, only the Nafion[®] NR50 gel showed significant activity enhancement in *p*-cresol. In order to gain insight into these relative catalytic activities, the acid capacity and accessibility of acid groups in these solid acid catalysts were studied using temperature programmed desorption/thermogravimetric analysis (TPD/TGA) techniques with isopropanol as probe molecule. The TPD/TGA studies show that the sulfonic acid groups are readily accessible to 2-propanol vapor in the 13 wt% Nafion[®] resin/SiO₂ composite but not in gel-type Nafion[®] resin and Amberlyst-15[®]. © 1996 Academic Press, Inc.

INTRODUCTION

There are many commercial processes that are currently catalyzed by concentrated homogeneous mineral acids. These reaction media are highly corrosive, and the processes often produce large volumes of chemically reactive waste streams. As a result, a clear opportunity exists for new technologies that can replace these processes with more environmentally friendly solid acids. Besides various zeolite catalysts, sulfonic acid cation exchange resins such as Amberlyst-15[®] have found increasing use in industrial applications of this kind, as solid acid substitutes for mineral

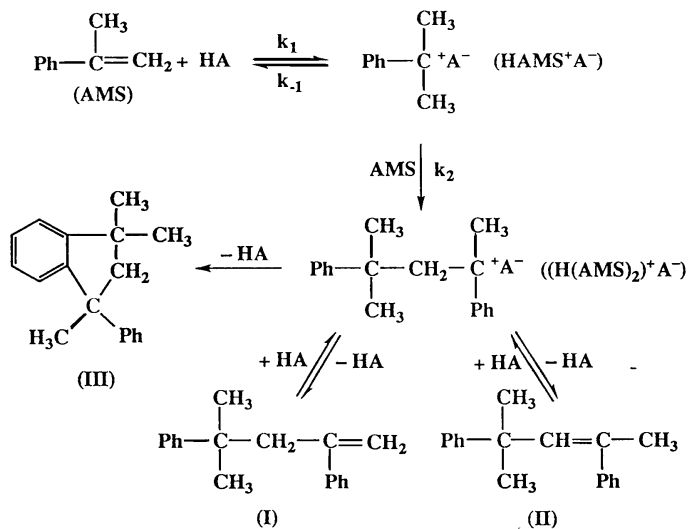
acids in reactions like hydration, etherification, and esterification of olefins, and condensations of carbonyl compounds (1–2). Another type of cation exchange resin, perfluorinated sulfonic acid resin (e.g., Nafion[®]), can also be used to catalyze many of these transformations, as has been well documented by Olah's group and other researchers (1, 3–5). Nafion[®] resin's advantages include: apparent stronger acidity, and higher thermal and chemical stability relative to macroporous sulfonic acid resins, but its disadvantages, including high cost and a low surface area gel-type structure, have prevented widespread adoption of Nafion[®] resin as a catalytic material. There have been several attempts to disperse Nafion[®] resin on higher surface area supports to increase the catalytic activity in nonswelling media (4, 6). These supported Nafion[®] resin catalysts showed improved performance in comparison with the corresponding bulk materials for hydrocarbon conversion processes such as alkylation of aromatics or isoparaffins with olefins, oligomerization or hydration of olefins, and so on; however, only modest dispersion of the acid resin on these supports could be obtained, and the long term stability of these catalysts has not been documented. Potential drawbacks include washing out of the Nafion[®] resin from the support by the solvent and reactant mixture when employed in the liquid phase.

We have recently described the preparation of a novel high surface area Nafion[®] resin/silica composite catalyst (7). In this new class of composite materials, Nafion[®] resin particles are encapsulated within a porous silica network, leading to both high Brønsted acid site densities and high surface areas. In this study we have examined the activity of this composite catalyst relative to a variety of other acid catalysts, both heterogeneous and homogeneous, for the α -methylstyrene dimerization. We have explored the chemistry in both polar and nonpolar solvents. We demonstrate that under some conditions, the sulfonic acid groups in the Nafion[®]-H resin/silica composite are much more readily accessible than they are in other catalyst microstructures, and this leads to significant activity enhancements.

Most of the published work on AMS dimerization is in the patent literature (8). Four dimerization products,

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2,4-diphenyl-4-methyl-1-pentene (I), 2,4-diphenyl-4-methyl-2-pentene (II), 1,1,3-trimethyl-3-phenylindane (III), and cis- and trans-1,3-dimethyl-1,3-diphenylcyclobutane (IV) have been reported. We observed only I–III under our reaction conditions (Reaction Scheme 1).

The unsaturated dimers of AMS, particularly 2,4-diphenyl-4-methyl-1-pentene (I), are industrially important and are useful as chain-transfer agents or molecular weight regulators in the production of polymers. Derivatives of the saturated dimer, 1,1,3-trimethyl-3-phenylindane (III), are used in the electronic industry as a liquid vehicle for inorganic particles. Dimers are produced by using mineral acid catalyst AlCl_3 (9). A BASF process that converts styrene to 1-methyl-3-phenylindane for the production of anthraquinone was catalyzed by mineral acids (10). Chaudhuri and Sharma have recently described the use of this reaction to compare the catalytic activity for a number of solid acids (8). When Nafion[®] resin was used, a strong solvent dependency of the dimerization rate constant was observed. We have extended the work of Chaudhuri and Sharma and included in the study the new Nafion[®]-H resin/silica composites. We have observed that the solvent effect is completely absent for these materials.

EXPERIMENTAL

Catalysts and Materials

The Nafion[®] resin/silica composite was prepared using an *in situ* sol-gel technique. The synthesis and detailed characterization of these materials have been described elsewhere and only a brief summary will be presented here (7). In a typical synthesis, a solution of partially hydrolyzed tetramethylorthosilicate (204 g of $\text{Si}(\text{OMe})_4$, 33 g of H_2O , and 3 g of 0.04M HCl) is rapidly mixed with a basic

solution of Nafion[®] resin (150 ml 0.4M NaOH added to 300 ml 5% Nafion[®] resin by weight, perfluorinated ion-exchange polymer available from Aldrich Chemical Company). The base induces rapid condensation of the silica and a hard gel is formed in seconds. The gel is then dried (at 90°C) and re-acidified with nitric acid (stir with 500 ml of 25% nitric for 1 h, filtered and washed with distilled water and repeated a total of four times). The resulting material is most accurately described as a nanocomposite wherein the Nafion[®] resin is distributed at the nanometer level (in the 20–60 nm range) within the porous silica network. The Nafion[®] resin loading in the composite material that we have used throughout this work is about 13 wt%; however, if desired this can be varied (up to about 80 wt%), by increasing the amount of Nafion[®] resin solution used in the general procedure outlined above.

Nafion[®] NR50 resin was obtained from the DuPont Company. The proton form has an acid capacity ~ 0.89 meq/g (5). It was used without further treatment. Amberlyst-15[®] was purchased from Rohm and Haas. This resin contains a small amount of free acid which could result in a much higher activity in the polar solvent *p*-cresol. This effect has also been noticed by Chaudhuri and Sharma (8). Therefore, the Amberlyst-15[®] catalyst was washed with an acetone and water mixture several times until a neutral solution was obtained. The washed catalyst has an acid capacity of 4.3 meq/g. The supported Nafion[®] resin employed here is Nafion[®] resin on shot coke which was prepared according to an earlier DuPont patent (6). The catalyst contains ~ 2 wt% Nafion[®] resin. Before testing, this catalyst was re-activated by stirring in a 25 wt% HNO_3 acid solution at 80°C overnight, followed by several washings with distilled water. Reactant AMS, solvents cumene and *p*-cresol, *p*-TSA and triflic acid were all purchased from Aldrich of the highest purity available. Dry molecular sieves were added to AMS and cumene to eliminate water in these samples.

Characterization of Solid Catalysts

The Nafion[®] resin/silica composite is a hard, porous, glass-like material. Individual particles are a few millimeters in size, with values of the BET surface area, pore diameter, and pore volume of $344 \text{ m}^2 \text{ g}^{-1}$, 9.8 nm, and 0.85 cc g^{-1} , respectively. The material could be crushed and sieved to desirable sizes for particular applications. The surface area is approximately 20,000 times greater than that of the pure polymer (Nafion[®] NR50 resin, with a surface area of about $0.02 \text{ m}^2 \text{ g}^{-1}$). The 2 wt% Nafion[®] resin on shot coke has a BET surface area $\sim 1 \text{ m}^2 \text{ g}^{-1}$ and a mean pore diameter of 100 nm.

TGA/TPD Measurement

Chemisorption and temperature programmed desorption of 2-propanol on the solid acids was studied using

a combined vacuum microbalance/mass spectrometer system. Samples are loaded onto the microbalance pan (typically 10 mg) and the system is pumped down to background pressures of $<10^{-7}$ torr with a turbomolecular pump. Gases are admitted into the chamber from an attached manifold. Pressures are measured with a Baratron capacitance manometer. Uptake is followed gravimetrically. Following adsorption, the system is reevacuated to background pressures. Residual strongly bound material is reflected in the mass increase. The temperature is ramped at $5^{\circ}\text{C}/\text{min}$ to 400°C . Mass spectral profiles of the evolving gases are followed with a UTI 100C quadrupole mass spectrometer. Details of this apparatus have been described previously (11).

Catalytic Reactions

The AMS dimerization reactions were carried out in a two-neck flask with magnetic stirring in solvents cumene or *p*-cresol at 50°C . For a typical run, 6 g of AMS was added to 54 g of solvent. Usually, between 0.1 to 1.0 g of solid acid catalyst was used for the reactions. Prior to reaction, all the solid acid catalysts were dried in a vacuum oven at 150°C overnight, except Amberlyst-15[®] which was dried in a vacuum oven at 110°C . Flasks used for carrying out the AMS dimerizations were also dried in a vacuum oven. Due to their extraordinarily high activities in *p*-cresol, the two soluble acids *p*-TSA and triflic acid were first dissolved in the solvent and then the acidic solutions were added to the reaction mixture. During the reaction, aliquots (~ 0.2 ml) were taken at certain time intervals and analyzed by GC and GC/MS for product quantification and identification, respectively. External standard was used for the GC analysis and good mass balances (better than 90%) were obtained by monitoring both the AMS converted and the dimers formed in the reaction mixtures. In *p*-cresol solution, besides the three dimers, a small amount of alkylation product formed by addition of AMS to *p*-cresol was also observed. In most cases this product amounted to less than 5% of the total product mixture. On the other hand, in cumene solution no significant amount of by-product was ever detected.

RESULTS

Reaction Kinetics

Figure 1 is a plot of AMS and product concentration versus time for the 13 wt% Nafion[®] resin/silica composite (0.5 g) catalyzed dimerization of AMS at 50°C in cumene. It appears that the unsaturated 2,4-diphenyl-4-methyl-1-pentene (I) is the kinetically favored product. It was the predominant product until AMS conversion reached $\sim 90\%$ in this case. The product distribution also depends on the catalyst, solvent, and reaction temperature employed. Low temperature favors the formation of product (I). In fact, when

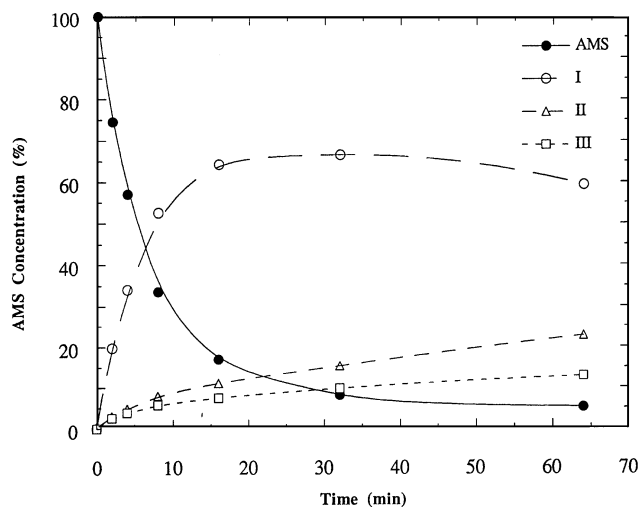


FIG. 1. AMS concentration (%) as a function of reaction time (min) when AMS (6 g) dimerization was carried out in cumene (54 g) at 50°C with 13 wt% Nafion[®] resin/silica composite catalyst (0.5 g).

the reaction was carried out at 0°C , a selectivity to dimer (I) of 92.4% at 93.0% AMS conversions can be obtained. Product (III) appears to be the thermodynamically favored product. At higher temperatures given enough reaction time, products (I) and (II) could both be converted to 1,1,3-trimethyl-3-phenylindan (III). At 50°C , Fig. 1 is very representative of most of the reaction systems we have examined.

Figure 2 is a plot of $\ln([\text{AMS}]_t/[\text{AMS}]_0)$ versus time for the same catalyst, 13 wt% Nafion[®] resin/silica composite (0.2 g), as in Fig. 1 but from a different experiment, where $[\text{AMS}]_t$ and $[\text{AMS}]_0$ are the AMS concentrations at time t and time zero, respectively. This plot shows excellent linearity. Reaction is clearly first order in AMS under these conditions as also observed by Sharma *et al.* (8). First-order rate

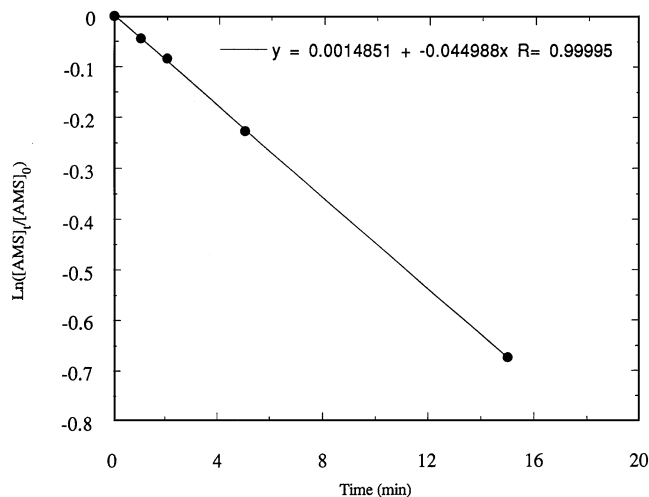


FIG. 2. Plot of $\ln([\text{AMS}]_t/[\text{AMS}]_0)$ versus reaction time (min) for AMS (6 g) dimerization in cumene at 50°C with 13 wt% Nafion[®] resin/silica composite catalyst (0.2 g).

constants are calculated from data of this kind using AMS conversions from 0–30%. For all catalysts, the reaction rate was independent of the stirring rate (200–1000 rpm). In addition, for the 13 wt% Nafion[®] resin/silica composite catalyst no particle size effect (9 to >80 mesh) was observed. These observations imply that diffusion limitations were not present under the conditions employed. When AMS dimerization was carried out with plain silica support, under the same reaction conditions, no AMS conversion was detected.

All of the first-order rate constants for AMS dimerization measured over various catalysts and in both cumene and *p*-cresol solutions are listed in Table 1. The acid capacities of the solid acids listed in Table 1 were determined by simple acid/base titrations, for which solid acid was first ion exchanged with large excess of sodium chloride (100/1 for Na⁺ to H⁺) and then the aqueous solution was titrated with volumetric NaOH standard after filtering out the solid catalyst and extensive washing with deionized water. The pK_a values of small organic acids listed here (12) are quite different from that of the Hammett acidity function ($-H_0$) values for these acids commonly cited in the literature (13). We have chosen to list these values because all of them were available from a single, self-consistent source. In the discussion that follows (*vide infra*) we will be mainly concerned with the relative proton donor abilities of these acids in polar media, and we feel that the values listed in Table 1 adequately capture this trend.

TABLE 1

First-Order Rate Constants for the Dimerization of α -Methylstyrene (AMS, 6 g in 54 g Solvent) over Solid and Homogeneous Acid Catalysts in Organic Solvents at 50°C and Properties of Acids

Catalyst	Solvent:		Acid properties		
	Cumene (1/meq H ⁺ · h)	<i>p</i> -Cresol	[H ⁺]	Surface area	pK_a^a
NR-50	0.1	2.3	0.89 meq/g	0.02 m ² /g	
Composite 13%Nafion [®] resin/SiO ₂	110.1	106.8	0.14	350	
Amberlyst-15 [®]	0.6	0.3	4.30	45	
2% Nafion [®] resin on Shot Coke	3.9	4.9	0.02	~1	
Glacial acetic acid	<i>b</i>	~0.0	6.67		4.8
Trifluoroacetic acid	<i>b</i>	1.0	8.77		-0.6
<i>p</i> -Toluene sulfonic acid (<i>p</i> -TSA)	<i>b</i>	1,200	5.26		-2.7
Triflic acid CF ₃ SO ₃ H	<i>c</i>	15,000	6.67		-5.5

^a pK_a values for these acids have also often been estimated using Hammett acidity function methods. The trends in relative acidity seem to be the same, although H_0 values are typically more negative.

^b These acids are insoluble in cumene solution and no activity were measured.

^c Triflic acid is very active, but its solubility is very low in cumene solution and therefore the activity could not be quantified.

The 13 wt% Nafion[®] resin/silica composite is the most active catalyst among the heterogeneous catalysts tested. Nafion[®] NR50 resin is not an efficient solid acid catalyst in the nonswelling solvent cumene for AMS dimerization. However, its activity is enhanced by over an order of magnitude in *p*-cresol. In contrast, the performance of the composite, the supported Nafion[®] resin catalyst, and Amberlyst-15[®] did not depend on the solvents used. Even though Amberlyst-15[®] has the highest acid capacity and a high BET surface area, it is not very active for the dimerization of AMS under the reaction conditions employed here. For Nafion[®] NR50 resin and Amberlyst-15 catalyzed AMS dimerization, the rate constants that we obtained are consistent with those reported by Chaudhuri *et al.* (8) at higher temperatures. In particular, the relative rate constants for Amberlyst-15[®] (in cumene), NR50 (in cumene), and NR50 (in *p*-cresol) are very similar, (1 : 0.06 : 3.6) versus (1 : 0.16 : 3.8).

We have also benchmarked the heterogeneous catalyst performance against several soluble acids. *p*-TSA does not dissolve in cumene and no AMS conversion was observed. However, it does dissolve in *p*-cresol and very high activity was observed in that solvent. With triflic acid, AMS dimerization can be observed in cumene, but due to its very low solubility the reaction rate could not be quantified. Triflic acid is an even more active catalyst than *p*-TSA in *p*-cresol. The weaker acid trifluoroacetic acid can also catalyze the dimerization in *p*-cresol, although it is considerably less active than *p*-TSA. Glacial acetic acid is not catalytically active. Table 1 lists estimated pK_a values for these acids. Although the Brønsted acid strengths of these molecules in *p*-cresol may not be the same as in water, the trend in activities follows pK_a , suggesting that the homogeneous catalysts act as specific acid catalysts in *p*-cresol. The pK_a of protonated *p*-cresol is about the same as that of the *p*-TSA (13). So one might expect nearly complete proton transfer from *p*-TSA or triflic acid to solvent in *p*-cresol. The lower activity of the weaker acids may reflect the lower concentrations of free protons.

DISCUSSION

A simplified version of Reaction Scheme 1 suitable for kinetic analysis is Scheme 2:

1. $AH + AMS \leftrightarrow (HAMS)^+A^-$
2. $(HAMS)^+A^- + AMS \rightarrow [H(AMS)_2]^+A^-$
3. $[H(AMS)_2]^+A^- \rightarrow \text{prod.} + AH$

Based on this reaction scheme, assuming k_3 is fast and applying a steady state approximation for $(HAMS)^+A^-$, one can derive the following expression for the rate of product appearance:

$$\text{Rate } (R) = k_1k_2[AMS]^2[AH]/(k_2[AMS] + k_{-1}) \quad [1]$$

This expression suggests two limiting kinetic regimes. When $k_2[\text{AMS}] \gg k_{-1}$, then the rate expression reduces to

$$R = k_1[\text{AMS}][\text{AH}]. \quad [2]$$

The rate should appear first order in AMS concentration, and the observed rate constant is the product of the elementary rate constant for formation of the carbenium ion, k_1 , and the effective acid catalyst concentration. On the other hand, when $k_{-1} \gg k_2[\text{AMS}]$ then the rate expression reduces to

$$R = Kk_2[\text{AMS}]^2[\text{AH}], \quad [3]$$

where K is the equilibrium constant for proton transfer between AMS and whatever the effective acid AH is. The first-order behavior of all of the acid catalysts (vide infra) suggests that we can rationalize their relative catalytic activities within the framework of Eq. [2].

In the case of the homogeneous acids it seems likely that the reaction is specific acid-catalyzed and that the proton donor is a solvated proton. This appears to be implicitly assumed by Beltrame *et al.* (14). It is suggested by the clear trend in rates with pK_a that we observe and is also consistent with the modest activity of oxalic acid ($pK_a \sim 1$) reported by Chaudhuri *et al.* in phenol (8). Since the effective proton donor is the protonated solvent, SH^+ , for all homogeneous acids, k_1 , k_{-1} , and k_2 in Eq. [1] will be independent of the nature of the added acid. Relative rates are then determined by the effective concentrations of SH^+ , fixed by a pre-equilibrium between the added Bronsted acid and *p*-cresol, i.e., $\text{CF}_3\text{COOH} + \text{S} \leftrightarrow \text{CF}_3\text{COO}^- + \text{SH}^+$, where S represents a solvent molecule. Assuming complete dissociation for the strongest acid, triflic acid, this interpretation implies that the equilibrium constant for the dissociation of *p*-TSA is about 0.2, and for TFA is about 4×10^{-3} in this medium. Furthermore, the entry in Table 1 for triflic acid represents the turnover frequency for the solvated proton within this set of assumptions, since $[\text{AH}] = [\text{SH}^+] = [\text{TFA}]_0$. This can be a benchmark for other proton sources.

It is clear from Table 1 that the same interpretation cannot be applied to the resin acids. The reaction cannot be specific acid catalyzed. The absence of a solvent effect for the supported catalyst, the Nafion[®] resin/silica composite and Amberlyst-15[®], suggests that these processes must be general acid catalyzed, with proton transfer occurring directly from the resin acid to AMS. Relative rates for different catalysts can then be described within the context of Eq. [2], where both k_1 , and the nature and concentration of the effective proton donor, AH will differ for each solid acid.

Let us consider first, the three Nafion[®] resin-based catalysts. The ratio of the observed first-order rate constants per acid equivalent in the nonpolar solvent, cumene, is 1.0/39/1100 for NR-50/supported/composite. We might begin by assuming that k_1 will be the same for these three

materials since the proton donor in all cases is a perfluoro-sulfonic acid residue. The relative rates then might be related to different numbers of accessible acid sites within the different microstructures. Under nonswelling conditions, we estimate the accessible acid site density from the number of sulfonic acid residues on the exterior surface of the Nafion[®] resin particulates. The ratio of the BET surface areas in 1.0/50/17500. Of course for the composite, most of the BET surface area is the noncatalytic, silica surface. Microscopy data suggests that in the Nafion/silica composite, the Nafion[®] resin is uniformly dispersed as 20–60 nm particulates within the silica matrix. Therefore if we presume that the Nafion[®] resin surface area in the composite is given by the weight fraction times the BET surface area, then the Nafion[®] resin surface area ratios would be 1.0/50/2280. For the supported catalyst this presumes that the Nafion[®] resin is well dispersed over the support. This ratio is very close to the relative rate ratio in cumene, although both the supported and composite materials appear to be a factor of 2 or so less active than this rough model suggests. It is quite likely that the Nafion[®] resin is not uniformly dispersed on the supported catalyst and that the weight fraction overestimates the Nafion[®] resin surface area fraction in the composite (15).

We can pursue this picture a little further by estimating the absolute number of acid residues on the external surface of Nafion[®] NR-50 resin. Assuming a bulk density of 2 g/cc, and a BET surface area of 0.02 m²/g we calculate that the fraction of sulfonic acid residues within the average acid–acid site separation distance of the surface is 4.0×10^{-5} , the so-called noninteraction accessibility suggested by Buttersack [16]. This implies that the activity/accessible acid site, or turnover frequency, for a sulfonic acid residue in Nafion[®] NR-50 resin is $0.1/4.0 \times 10^{-5} = 2500 \text{ h}^{-1}$. This is about a factor of 6 lower than we estimated above for the solvated proton in homogeneous media and suggests that the sulfonic acid residues in Nafion[®] resin have a high inherent activity even in nonsolvating media. This is consistent with previous work comparing structurally identical sulfonic acid sites in heterogeneous and homogeneous acids which shows similar but slightly lower enthalpies for proton transfer from the solid acid systems to a variety of bases (17).

From this point of view, we may look at the composite as a way of increasing the accessible fraction of acid residues by stabilizing Nafion[®] resin spheres of approximately 30-nm radius. Since the specific surface area of a collection of uniform spheres is given by $S = 3/rp$, where r is the radius and p is the bulk density, then we would expect that decreasing a sphere radius from 75 μm in NR-50 resin to 30 nm in the composite, the number of surface accessible sites would increase by about 2.5×10^3 . We observe a rate increase of about 1100 in cumene. Again, the estimated increase in accessible sites is likely to be high, since the spheres are

embedded in the silica matrix and the surfaces cannot be fully available to the substrate. This argument also does not consider the possibility that the AMS concentration in contact with the Nafion[®] surface within the composite might be different from the solution concentration. However, because of the structural similarity of AMS and cumene we would not expect the partitioning to be large. On balance, the simple surface-area based accessibility arguments appear to give a reasonable semiquantitative rationalization of the relative activities of this set of catalysts.

We can apply the same analysis to Amberlyst-15[®] catalyst. Using the BET surface area (45 m²/g) and the assumptions applied to Nafion[®] NR-50 resin above, we calculate that the fraction of acid sites accessible from the external medium should be 3.9×10^{-2} in Amberlyst-15[®] (16). This implies an activity/external acid site in cumene of 15. This is a factor of 266 lower than our estimated turnover number for Nafion[®] resin. Taken at face value, as the ratio of k_1 values for the two types of solid acid sites present in these resins, it could be interpreted as reflecting differences in the acid strength between the benzene sulfonic acid-like residues in Amberlyst-15[®] and the perfluoroalkanesulfonic acid-like residues in Nafion[®] resin. However, we are uncertain that the BET surface area has much relevance to the actual surface area presented to the medium by the macroporous Amberlyst-15[®] resin in any solvent. So while we believe that this analysis may offer some insights into the factors affecting activity for a given resin in different microstructures, as for the case with Nafion[®] resin preparations above, we are reluctant to attach much quantitative significance to this type of comparison when it is extended to different resins where the interactions with solvent might be very different.

Solvent swelling of resin catalysts is another means of increasing the effective number of acid sites. In the polar solvent, *p*-cresol, the rate with NR-50 resin increases by a factor of 23, the rate for the supported catalysts increases by 20% and the rate with the composite is essentially unchanged. Perhaps most surprising, the rate for Amberlyst-15[®] is more or less unchanged. Although we have not measured the equilibrium swelling of these catalysts in *p*-cresol, it would be hard to rationalize these results if the only role of the solvent were to increase the number of acid sites that are available to AMS. For example, we observe slight reductions in activity for Amberlyst-15[®] and the composite, implying that solvents can also affect the proton transfer rate constant, k_1 . This would not be unexpected, since a solvent molecule on either side of the equilibrium in the first step of Scheme 2 will surely change the overall thermochemical driving force for proton transfer (17). Perhaps when the noninteraction accessibility is low, as in NR-50 resin (0.0025%) the enhancement in the number of accessible sites is the dominant factor, but when the noninteraction accessibility is high as in Amberlyst-15[®] (4%) or the com-

posite (12%, based on uniform 30 nm spheres), *p*-cresol acts principally to stabilize the undissociated active sites through hydrogen bonding and thereby reduces the overall catalytic activity.

We have carried out another type of experiment that tries to tie these swelling and acid site accessibility arguments together. The basic experiment is described in the Experimental section. Briefly, 5–50 mg of catalyst is placed in the pan of a microbalance enclosed within a high vacuum chamber. The sample is dehydrated by mild heating in a vacuum and stabilized in a vacuum at background pressures of $<10^{-7}$ torr. The sample is then exposed to adsorbate vapor at room temperature and the uptake is followed continuously as the sample weight increases. After saturation is reached, the chamber is evacuated and a residual strongly bound mass is retained on the catalyst. Finally, the system is heated and the mass falls as chemisorbed material is desorbed. The partial pressures of desorbing products are followed by mass spectroscopy during this phase. A typical TGA profile and the changes in mass spectral intensities for selected masses during TPD are shown in Fig. 3 for 2-propanol as adsorbate on the 13 wt% Nafion[®] resin/silica composite catalyst. Notice the rapid uptake rates, the stable residual mass, and the clean desorption profiles for *m/e* 41 and *m/e* 18. *m/e* 41 and 18 are used to track the desorption of propene and water, respectively. For this catalyst, all of the mass loss during temperature programmed desorption can be accounted for as propene and water. Results of this experiment (10 torr 2-propanol; 23°C) carried out on all four of the heterogeneous acid catalysts are compared in Table 2.

We use time to half-saturation to characterize the adsorption kinetics, although the uptake process is not strictly first order. The pure resin catalysts, both Nafion[®] NR-50 resin and Amberlyst-15[®], are much slower to reach saturation than the supported or composite catalysts. The saturation uptakes also vary widely. It is interesting that with all of the Nafion[®] resin catalysts, the saturation uptakes exceed what would be required for a stoichiometry of one adsorbed

TABLE 2

Summary of TGA/TPD Data

Sample	Uptake t(1/2) (min)	Uptake sat. (g/g)	Residual mass (mmol/g)	[H ⁺] (meq/g)	TPD ^a
NR-50	15	0.73	0.80	0.89	69, 57, 43, 41, 18
13% Nafion [®] resin/silica	2	0.99	0.09	0.14	41, 18
2% Nafion [®] resin on shot coke	1	0.0051	0.01	0.02	57, 43, 41, 18
Amberlyst-15 [®]	22	0.154	0.26	4.30	64, 48, 41, 18

^a Principal *m/e* values displaying significant intensity in the desorption spectrum.

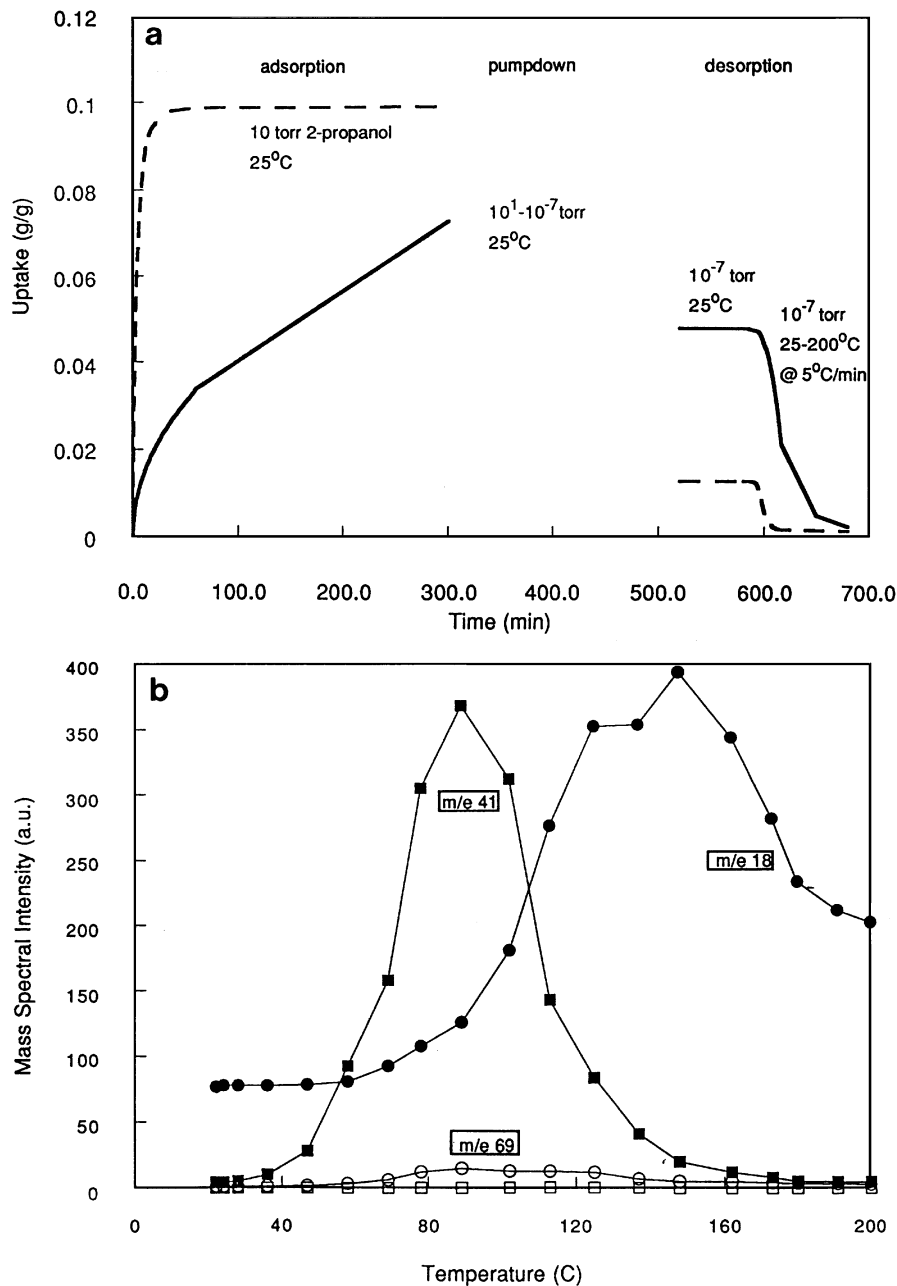


FIG. 3. (a) Weight changes during adsorption/temperature programmed desorption of 2-propanol on 13% Nafion[®] resin/silica catalyst (dashed line) and Nafion[®] NR50 resin beads (solid line). (b) Mass spectral profiles for m/e 41, 18, and 69, during TPD for 13% Nafion[®] resin/silica composite.

2-propanol/acid equivalent, but with Amberlyst-15[®] it is only about 0.5 of this value. On reevacuation of the TGA chamber, the residual masses of 2-propanol, the chemisorbed amount, is close to the expected acid site concentration for the Nafion[®]-based catalysts, but only about 5% of that amount for Amberlyst-15[®]. Finally, on temperature-programmed desorption to 150°C, while the composite catalyst yields only propene and water, the products of unimolecular dehydration (Fig. 3b), the NR-50 resin shows significant amounts of higher mass fragments pre-

sumably due to oligomerization reactions of propene during the slow diffusion out of the catalyst bulk. Amberlyst-15[®] yields nearly complete conversion to propene and water, but above 125°C significant amounts of SO and SO₂ are also evolved.

These results clearly illustrate the differences in accessibility of chemisorption sites, presumably Brønsted acid sites, among these materials at least for adsorption from the gas phase at low temperature and pressure. The easy access to strongly binding active sites in the composite catalysts

correlates well with the high solvent-independent activity of this catalyst in the AMS dimerization. It illustrates the promise of this family of catalysts for Brønsted acid catalyzed chemistry in nonpolar and gas phase environments.

CONCLUSIONS

First-order rate constants for the AMS dimerization catalyzed by heterogeneous solid acids as well as soluble organic acids were determined in the liquid phase. Very high activity was obtained from the highly porous 13 wt% Nafion[®]-H resin/silica composite catalyst. It exhibited more than two orders of magnitude higher activity than the bulk Nafion[®]-H resin. The 2 wt% Nafion[®] resin on shot coke was significantly more active than the plain Nafion[®] resin catalyst as well. Amberlyst 15[®] was roughly a factor of 200 less active than the composite on an acid equivalent basis, about a factor of 7 less active on a weight basis.

A strong correlation is found between the catalytic activity of these heterogeneous catalysts for the AMS dimerization and the accessibility of their Brønsted acid groups. For example, Nafion[®] NR50 resin show very low activity in the nonpolar media and enhanced activity was observed in polar solvent which is a result of framework swelling by the solvent and increased acid accessibility. This enhancement in accessibility can be made solvent independent by incorporating the Nafion[®] resin into a silica matrix. Because of the importance of solvent effects, BET surface area alone may not be a good indicator of accessibility. In particular, even though the BET surface area of the Amberlyst-15[®] is very high (45 m²/g), both catalytic and TGA data indicated that the accessibility of the acid group is significantly lower than that in the Nafion[®] resin/silica composite material. We believe that the enhancement in accessibility, combined with the inherent advantages of Nafion[®] perfluoro-sulfonic acid resins as a solid acid source (high acid strength,

thermal stability, chemical inertness), make the Nafion[®]-H resin/silica composites very attractive materials for a variety of solid acid catalyzed processes.

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