mental calibration curves and toluene as an internal standard.

For preparative purposes, higher concentrations of mesoxalate (8.5 mmol) and alkene (10.5 mmol) in 3 mL of $CCl_4$ were used. The reactions were conducted at 1 bar in stainless-steel tubes (temperatures and yields given below). After the reaction, the solution was diluted, unreacted dimethyl mesoxalate was hydrolyzed with water, and the organic phase was dried over $MgSO_4$ overnight. After removal of the solvent, the liquid residue was placed onto silica gel (Merck, 70–230 mesh) in a 30 × 15 cm column and eluted with petroleum ether–ethyl acetate (95:5).

All adducts were colorless liquids. Adducts 1 and 2 were analyzed previously;[10] however, spectral results were missing. The structures of the new adducts (3–5) were based on spectral data and established by comparison with the structures of 1 and 2.

**Adduct 1 (*Z* + *E*):** obtained at 130 °C, 24 h; 95% yield; GC, 2 peaks in a 7:3 ratio; IR 3500 (OH), 1745 (C=O), 1620 (C=C); $^1$H NMR ($CCl_4$) δ 5.85 (dt, 1, CH=CHCH$_2$), 5.50 (dt, 1, CH$_2$CH$_2$CH=C), 3.79 (s, 6, OCH$_3$), 2.70 (d, 2, C=CHCH$_2$), 2.01 (dq, 2, CH$_2$CH$_2$), 1.40 (m, 2, CH$_3$CH$_2$), 0.90 (t, 3, CH$_3$).

**Adduct 2 (*Z* + *E*):** obtained at 140 °C, 18 h; 95% yield; GC, 2 peaks in a 9:1 ratio; IR 3500 (OH), 1735 (C=O), 1625 (C=C); $^1$H NMR ($CCl_4$) δ 5.10 (t, 1, CH$_3$C=CHCH$_2$), 3.78 (s, 6, OCH$_3$), 2.78 (d, 2, C=CHCH$_2$), 2.00 (m, 2, CH$_3$CH$_2$), 1.60 (s, 3, CH$_3$C=C), 0.90 (t, 3, CH$_3$).

**Adduct 3:** obtained at 140 °C, 15 h; 70% yield; GC, 1 peak, $t_R$ = 18.8 min; IR 3500 (OH), 1730 (C=O), 1625 (C=C); $^1$H NMR ($CCl_4$) δ 4.95 (d, 2, CH$_2$=C), 3.75 (s, 6, OCH$_3$), 2.82 (s, 2, C=CCH$_2$), 2.01 (s, 2, (CH$_3$)$_3$CCH$_2$), 0.90 (s, 9, CH$_3$). Anal. Calcd for $C_{13}H_{22}O_5$: C, 60.44; H, 8.58; O, 30.97. Found: C, 60.24; H, 8.68; O, 31.03.

**Adduct 4:** obtained at 120 °C, 22 h; 90% yield; GC, 2 peaks in a 3:2 ratio, $t_R$ = 19.5 [(*E*)-4], 20.6 min [(*Z*)-4]; IR 3500 (OH), 1730 (C=O), 1660 (C=C) [(*Z*)-4], 1625 (C=C) [(*E*)-4]; $^1$H NMR ($CCl_4$) δ 5.50 and 5.35 (m, 1, *J* = 7 Hz [(*Z*)-4], 18 Hz [(*E*)-4], CH=C), 3.80 (s, 6, OCH$_3$), 2.88 and 2.72 (s, 2, C=CCH$_2$), 2.02 (q, 2, CH$_3$CH$_2$C=C), 1.62 (d, 2, CH$_3$C=C), 0.97 (t, 3, CH$_3$). Anal. Calcd for $C_{11}H_{18}O_5$ (4, *Z* + *E*): C, 57.38; H, 7.88; O, 34.74. Found: C, 57.31; H, 7.76; O, 34.68.

**Adducts 5a + 5b:** obtained at 140 °C, 18 h; 100% yield (2:3 5a/5b). Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88; O, 34.74. Found: C, 57.28; H, 7.57; O, 35.03.

**Adduct 5a.** GC, 1 peak, $t_R$ = 15.4 min; IR 3500 (OH), 1740 (C=O), 1620 (C=C); $^1$H NMR ($CCl_4$) δ 3.78 (s, 6, OCH$_3$), 2.90 (s, 2, C=CCH$_2$), 1.65 (s, 9, CH$_3$C=C).

**Adduct 5b.** GC, 1 peak, $t_R$ = 16.4 min; IR 3500 (OH), 1740 (C=O), 1620 (C=C); $^1$H NMR ($CCl_4$) δ 4.88 (d, 2, CH$_2$C=C), 3.78 (s, 6, OCH$_3$), 2.81 (s, 2, C=CCH$_2$), 2.30 (m, 1, CH—C=C), 1.00 (d, 6, CH$_3$).

**Partial Molar Volumes.** Precision density measurements permit the apparent molar volume $\Phi_V$ to be determined according to the known equation

$$\Phi_V = \frac{M_w}{d_0} - \frac{d - d_0}{d_0}\frac{1000}{C}$$

in which $M_w$ is the molecular weight of the solute and $C$ its molar concentration and where $d$ and $d_0$ are the densities of the solution and the solvent, respectively. Over the examined concentration range, the $\Phi_V$ values were constant within experimental error.

Density measurements were performed with a digital densimeter (Sodev Model 02D) based on the model of Kratky and al.[29] The partial molar volumes were found as in Table IV (at 25.11 °C in $CCl_4$ as solvent) (±0.1–0.3 mL/mol).

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# Nafion-Catalyzed Photoreaction. Photoisomerization of 3-Methylene-1,2,4,5,6,6-hexamethylcyclohexa-1,3-diene[1]

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The heptamethylbenzenonium cation 2 was shown to be produced when a $CH_2Cl_2$ solution of 3-methylene-1,2,4,5,6,6-hexamethylcyclohexa-1,3-diene (1) is brought into contact with "anhydrous" Nafion in its acid form. Treatment of the Nafion with methanolic sodium hydroxide regenerates 1. Under the conditions used here, the number of active sites on the Nafion was found to be 0.347 mmol/g. Irradiation of the Nafion with light of wavelength greater than 380 nm caused 2 to be converted mostly to vinylcyclopentadiene 5, with minor amounts of pentamethylcyclopentadiene and hexamethylbenzene also being produced. No photoisomerization of 1 took place when it was irradiated under the same conditions in the absence of Nafion. The quantum efficiency for the conversion of 2 adsorbed onto the Nafion was found to be 0.48 ● 0.05; the same value as is found for the isomerization of 2 in homogeneous solutions. The product 5 could be displaced from the Nafion by more 1. This permitted the reaction to be carried out in a continuous mode with the Nafion functioning as a photocatalyst for the process.

Over the past few years, many photoreactions of carbenium ions and protonated carbonyl compounds have been reported.[3,4] In strongly acidic media, where the

reactants and photoproducts are stable as carbocations, the most commonly observed type of reaction are photoisomerizations. Frequently these photoisomerizations are very clean reactions, give rise to different products than those obtained from the neutral precursors of the carbocations, and are relatively efficient. As such, the photoreactions of carbocations are attractive from a preparative

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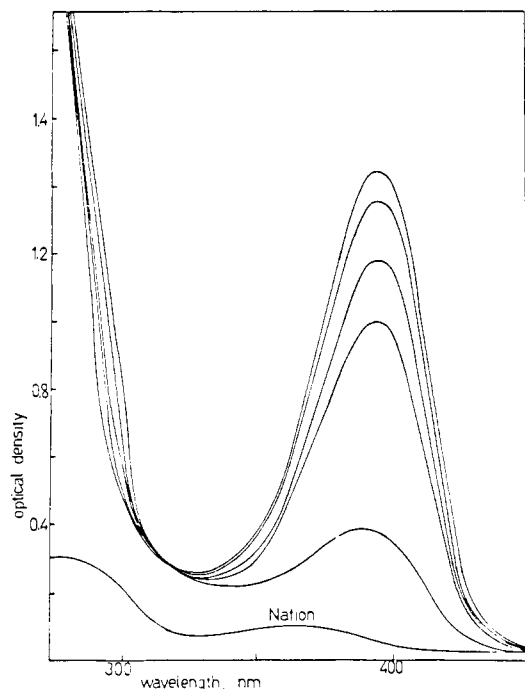(4) Childs, R. F. *Rev. Chem. Intermed.* 1980, *3*, 285.

**Figure 1.** Absorption spectra of 1 absorbed in Nafion.

point of view. However, their practical utility is seriously diminished by the use of strong acid solvents and the difficulty of recovering high yields of organic materials on neutralization of these acids.

In order to circumvent this detraction, we have investigated the use of heterogeneous acids in these photoreactions. The basic idea was to bring into contact a solution of the neutral precursor of the carbocation in an inert solvent with a catalytic amount of a strong acid in another phase. The adsorbed and protonated substrate could then be photoreacted and the photoproducts then displaced from the acid phase by more starting material. It would be particularly convenient from a separative point of view if the acid were in the solid phase.

There are several reports of the use of solid acidic materials to modify the light-absorbing properties and, in some cases, the photochemistry of organic materials.[5-7] However, in those systems studied it frequently is not clear whether complete protonation (or complexation) has occured. The problem is compounded by the similarity of the UV spectrum of the free and adsorbed species which frequently makes it difficult to determine just what is the nature of the species undergoing photoreaction.

In this present study by the appropriate choice of solid acid, organic substrate, and wavelength of the light used, we have been able to show that it is possible to carry out an acid-catalyzed photoreaction which involves a fully protonated species.

## Results and Discussion

The acid catalysts used in this study were Nafion-125 membrane and Nafion-501 beads in their acid form. Na-
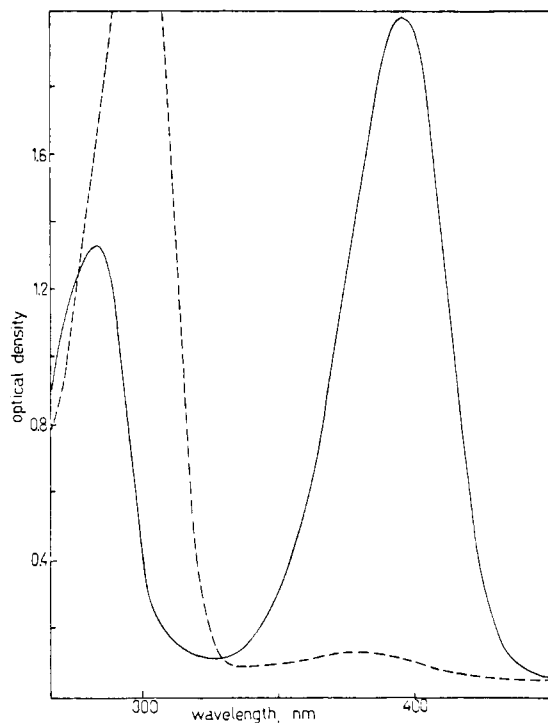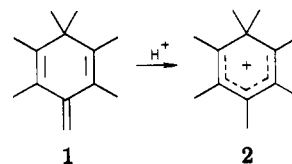


**Figure 2.** Photoisomerization of 1 on Nafion. Before irradiation, —; after irradiation for 15 min at 380 nm, ---.

fion is a perfluorinated acid resin with the acid groups being on $-(OCF_2CF(CF_3)_n-O-CF_2CF_2SO_3H$ side chains attached to a perfluorcarbon backbone. In its "anhydrous" form, as used in this work, Nafion is a strong acid with an $H_0$ value of $<-6$.[8] As can be seen from the lowest trace in Figure 1, the dried $CH_2Cl_2$-swollen membrane is almost transparent in the region with very weak bands being exhibited at 280 and 360 nm. These weak bands resemble the ones reported by Lee and Meisel for wet Nafion-120 membrane and likewise are probably due to an impurity in the membrane.[10]

The organic compound used in this study was the hydrocarbon 1.[11] Triene 1 is sufficiently basic to be com-

pletely protonated in 4 M HCl, and the dried Nafion used here should be sufficiently acidic to protonate 1. The neutral hydrocarbon exhibits a maximum in its UV spectrum at 256 nm (log $\epsilon$ 4.35).[12] On the other hand, the heptamethylbenzenonium ion (2) formed on protonation of 1 in $H_2SO_4$ posesses strong absorption bands at 400 and 288 nm (log $\epsilon$ 4.04 and 3.86, respectively).

The absorption of 1 by Nafion was conveniently monitored by UV spectroscopy. An absorption at 396 nm was rapidly formed when a $CH_2Cl_2$-swollen, "anhydrous" membrane was treated with a solution of 1 in $CH_2Cl_2$ (Figure 1). Removal of excess 1 by washing the membrane with $CH_2Cl_2$ gave a spectrum of the adsorbed material

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(8) Our measurements on the Nafion used in this work indicates an $H_0 < -6.5$. Nafion is expected to be considerably more acidic than this.[9]
(9) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Science* **1979**, *206*, 13.
(10) Lee, P. C.; Meisel, D. *J. Am. Chem. Soc.* **1980**, *102*, 5477.
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Table I. Photoreaction of 1 in the Presence of Nafion [a]

| time of irradn, h | % products | | | |
|---|---|---|---|---|
| | 1 | 5 | 6 | 7 |
| 0 | 99.6 | | | 0.4 |
| 2 | 69.7 | 26.8 | 0.8 | 2.7 |
| 4 | 38.8 | 57.2 | 0.9 | 3.1 |
| 6 | 17.9 | 77.8 | 1.0 | 3.3 |

[a] Anhydrous Nafion, $CH_2Cl_2$ as solvent.

exhibiting peaks at 396 and 283 nm (Figure 2). The extinction coefficients of these two bands (log $\epsilon$ 3.93 and 3.75, respectively) were obtained by averaging the optical density measurements of the membrane in various places and repeating the experiment several times. Good reproducibility was found provided oxygen was removed from the system. The UV spectrum of 1 absorbed on Nafion corresponds very closely with that of 2 in solution, indicating that 1 is essentially completely protonated on Nafion. The triene could be quantitatively recovered from the membrane by treating it with methanolic sodium hydroxide solution.

The number of active sites on the beads under the conditions used here was estimated by bring into contact a weighed sample of the powder with excess 1 in $CH_2Cl_2$. Absorption was monitored by quantitatively measuring the drop in concentration of 1 in the solution and subsequently by liberating 1 from the washed Nafion beads. In both cases the number of active sites was found to be 0.347 ± 0.002 mmol/g of beads. This value is considerably lower than that quoted for Nafion-501 powder and probably reflects the limited swelling of Nafion in $CH_2iCl_2$.

**Photoisomerization.** Hart and co-workers[13] have reported that the direct irradiation of 1 with short-wavelength light causes it to isomerize to 3. In this work, all



1          3
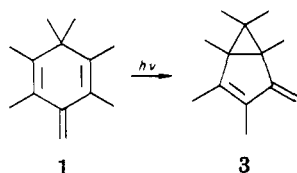
irradiations were carried out with light of wavelength greater than 380 nm, and, not surprizingly in view of the UV spectrum of 1, no photoisomerization of 1 could be detected under these conditions.

On the other hand, benzenium ions are known to isomerize when irradiated at longer wavelengths.[14,15] Thus 2 is converted to 4 on irradiation at 400 nm. The bicyclic



2          4
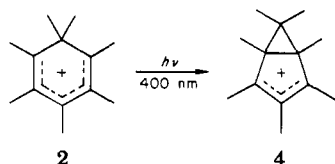
cation 4 is thermally unstable at room temperature and reverts to 2.[14] The rate of this isomerization appears to be independent of solvent.

Irradiation of 2 absorbed onto Nafion membrane either at low or room temperature caused the same result, an irreversible loss of the absorption band at 396 nm (Figure

2). A new band was formed centered at 297 nm. This new band did not correspond to that expected for 4, and the reaction was not reversed on standing at room temperature.

In order to identify the photoproduct(s), the reaction was carried out on a larger scale by using a stirred suspension of Nafion beads in $CH_2Cl_2$. The reaction was monitored by GC. The products were shown to be 5–7.



1          5 (95%)     6 (1%)     7 (4%)
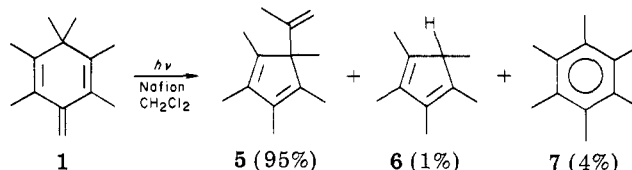
Of these products, the major compound was the cyclopentadiene 5 (Table I). The identity of 5 was established by comparison of its properties with those reported previously.[16] Hexamethylbenzene is very readily formed from 1 on standing, particularly in the presence of acid, and probably represents a dark side reaction. Compound 5 is known to be converted to 6 in aqueous acids, and 6 is probably formed as a result of trace amounts of water left on the Nafion.[17]

The formation of 5 could be accounted for by an initial photoisomerization of 2 adsorbed on the Nafion to the bicyclic cation 4. Proton loss from 4 could occur to give either 3 or 5. Both Hart[16] and Criegee[18] have shown that 4 and related homofulvenes readily isomerize to the more thermodynamically stable vinylcyclopentadienes. Independent experiments showed that 5 was not protonated by the Nafion under the conditions used here.

The quantum yield of the conversion of 2 absorbed on the Nafion membrane was measured by using a UV method. The quantum yield was found to be 0.48 ± 0.05 which corresponds within experimental error to the value of 0.45 ± 0.04 found in homogeneous acid solutions at low temperatures.[19] The similarity in these two quantum yields means that if 4 is the initially formed photoproduct, the rate of proton loss from 4 must compete very favorably with the reverse thermal isomerization of to 2.

The photoreaction of 1 can also be carried out with a hydrated Nafion catalyst and methanol as a solvent. In this case the products were 5 (19%), 6 (44%), 7 (15%), and some 20% of other unidentified volatile materials. The very much higher proportion of 6 produced confirms the suggestion that its production under the "anhydrous" conditions used above with $CH_2Cl_2$ as the solvent is due to traces of water retained in the membrane. The products obtained by using the hydrated membrane correspond more closely with those obtained by using homogeneous aqueous acid solvents, suggesting that a similar series of reactions is occurring in both cases.

In the experiment with the Nafion beads described above, it is important to note that the amount of 1 photoisomerized exceeded the number of active sites on the membrane by almost a factor of 3. This means that it is possible to displace the photoproduct 5 from the Nafion by the starting material 1. The quantum efficiency measured above referred to the reaction occurring just of absorbed species on the membrane. For this type of reaction to be practical the rates of diffusion of substrate onto and

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(19) Childs, R. F.; Goyal, A. K., unpublished results.

of product from the Nafion also have to be considered. While we do not have a quantitative measure of these at this time, it is clear from this catalyzed experiment that these steps occur at reasonable rates.

After the photoreaction was completed, it was possible to remove the solvent containing the photoproducts from the Nafion and replace it with another solution containing 1. Continued irradiation caused this additional material to be isomerized. It was noted that the Nafion became darkly colored as the reaction proceeded, and it would appear that some material was lost. However, the Nafion can be considered as a photocatalyst for the reaction, functioning by protonating the organic substrate. It remains to be seen how general this type of reaction will be.

## Experimental Section

UV spectra were obtained with a Pye Unicam SP8-100 spectrophotometer. Gas chromatography was performed on a Varian 3700 instrument coupled with a Varian CDS 111 integrator. The column used was a 5 ft × $^1/_8$ in. stainless-steel column packed with 5% OV-17 on Chromosorb W.

**Materials.** Nafion-125 membrane and Nafion-501 powder were obtained from Du Pont. The resins were conditioned by subjecting them to a number of alternating treatments with 5% NaOH and 20% HCl solutions. Between cycles the samples were thoroughly washed with distilled water and occasionally with methanol. The membrane and powder in their acid form were air-dried at 60–70 °C and subsequently further dried under vacuum at 80 or 110 °C for 24 h. The dried samples were stored in sealed containers over $P_2O_5$. All subsequent manipulations of the Nafion were carried out in a dry nitrogen atmosphere. The thickness of the dried and $CH_2Cl_2$ swollen membrane was 0.130 ± 0.005 mm in each case. The density of the membrane was found to be 1.932 (dried) and 1.962 g/cm³ (swollen).

**3-Methylene-1,2,4,5,6,6-hexamethylcyclohexa-1,4-diene (1)** was prepared according to previously described proceedures.[20]

**UV Experiments with the Membrane.** A rectangular membrane sample (0.8 × 3.0 cm), which had been previously swollen with $CH_2Cl_2$, was weighed and placed in a tightly stoppered UV cell and a UV spectrum recorded. The membrane was treated with a solution of 1 in $CH_2Cl_2$ of known concentration (ca. 0.001 M) for 0.5 h. Typical spectra obtained during this period are shown in Figure 1. The membrane was subsequently washed with fresh $CH_2Cl_2$ until no further change occurred in the UV spectrum (Figure 2). The amount of 1 absorbed by the membrane was determined by measuring the amount of 1 left in the initial $CH_2Cl_2$ solution by UV spectroscopy. The optical density of the membrane at several positions was measured for the maxima of the two bands. The optical densities were corrected for the absorbance of the membrane. The membrane sample volume was calculated from its weight and density measured above. The thickness of the membrane was used as the path lengths. The absorption maxima and extinction coefficients measured by this method are quoted earlier in the text. This experiment was repeated a number of times and a reproducibility of ±10% was found.

**Quantum Yield Determination.** An optical bench setup was used in the determination of the quantum yield. The light source was an Osram XBO 150W/S xenon lamp. Corning filters No. 3850 and 5970 were used to obtain a reasonably monochromatic light with maximum intensity at 350 nm. A quartz plate was used to split the light beam, and ferrioxalate actinometry was used.[21] A $CH_2Cl$-swollen membrane sample was treated with a solution of 1 until the absorbance at 396 nm had an optical density close to 2. Excess unprotonated 1 was removed by washing the membrane with $CH_2Cl_2$. The reaction occurring on the membrane with irradiation was quantitatively followed by monitoring the drop in the optical density of the absorption band at 396 nm with the extinction coefficient determined in the previous experiment. This experiment was repeated three times, giving values for the quantum efficiency of 0.43, 0.49, and 0.52, with a mean value of 0.48 ± 0.05.

**Preparative Reaction.** Nafion powder (2.505 g) was stirred in a test tube with 10 mL of a 0.178 M solution of 1 in $CH_2Cl_2$. The sealed tube was irradiated with a Phillips SP 500-W lamp fitted with water and a Corning glass filter (No. 3850). The test tube was stirred with a magnetic stirrer at such a rate that the Nafion was held in suspension. The course of the photoreaction was monitored by gas chromatography with naphthalene as an internal standard (the detector response for the various products and naphthalene was measured independently). The results are given in Table I. Addition of more $CH_2Cl_2$ solution of 1 to the Nafion recovered from the above reaction and continued irradiation led to the formation of more photoproducts.

An identical procedure was used with hydrated (undried) Nafion powder and a solution of 1 in $CH_3OH$. The composition of the products is given in the text.

**Measurement of the Number of Active Sites of Nafion.** A weighed sample of the powder (0.9932 g), dried as described above, was treated with 10 mL of a 0.0973 M solution of 1 in $CH_2Cl_2$ at -25 °C. The uptake of 1 by the Nafion was followed by GC analysis, with naphthlene being used as an internal standard. The reaction was followed for 16 h, after which time no further change could be detected. Under these conditions the number of active sites was found to be 0.343 mmol/g of Nafion powder.

In an additional experiment, 1.4093 g of the powder was treated with 10 mL of a 0.1373 M solution of 1 in $CH_2Cl_2$ at room temperature for 24 h. The treated powder was washed with fresh solvent until no further 1 could be detected in the wash solutions by GC analysis. The washed powder was treated succesively with three 25-mL portions of a 0.1 M solution of NaOH in methanol. The combined methanol solutions were evaporated in vacuo, and the residue was extracted with ether (25 mL). The ether solution was washed with water and dried (MgSO₄), and the resulting solution was analyzed by GC with naphthalene as an internal standard. The volatile products consisted of 1 (98.4%) and 7 (1.6%). The number of active sites corresponded to 0.348 mmol/g of Nafion powder.

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