# Acidic Properties of Functionalized Silica-Supported Polymers: Relation Between Reactivity and Morphology

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ABSTRACT: To improve and extend the properties of organic polymer-supported catalysts, the corresponding functional polymers were grafted on porous silica. Mechanical stability and constant shape, which are independent of solvent nature, and the possibility of modulating polarity to fit that of the reagents are new advantages. After a study of the grafting mechanism to understand the extent of grafting and chain length control, we tried to determine the optimal catalyst structure. Styrene was polymerized in the presence of a trifunctional silanoxy chain transfer agent in various amounts and was reacted with silica and then sulfonated. The acid catalytic properties of the resulting materials were evaluated in three tests of interest and were compared to those of reference materials. Selectivity was excellent. Reactivity was dependent upon catalyst compatibility with the reagents and the presence of water, which alters stability. Reactivity was poor for toluene alkylation, moderate for $t$-butanol dehydration, and good for ketalization. The specific activity was higher for a high number of short chains than for a low number of long chains at a given polymer to silica ratio. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65**: 2557–2565, 1997

Key words: supported polymers catalysts; silica-supported functional polymers; acidic polymer catalysts reactivity, selectivity, and morphology; toluene alkylation acid catalysis; alcohol dehydration acid catalysis

## INTRODUCTION

Polymer-supported catalysts have general interest from a practical point of view or on a scientific basis.[1–3] For instance, reactivity and selectivity may be varied according to morphology and nature of support for a same amount of active sites. This is due to a particular site distribution and environment. Our first approach was the synthesis of pure organic materials in various ways; a second approach was the combination of different parts of the former strategy and use of the complementary properties of inorganic supports. The organic networks (ion-exchange type, crosslinked styrene as basic monomer) were prepared by suspension polymerization with many improvements such as the use of polymer porogen or postcopolymerization for functionalization.[4] The second set of compounds were prepared by free-radical polymerization in the presence of silica or by grafting polymer on it.[5–8] Catalytic properties were measured.[9,10]

Two strategies for grafting an active precursor (vinylchlorobenzene or styrene) were used to obtain these materials: reacting a coupling bifunctional agent with the hydroxy groups of the silica, the other end being active (in transfer, copolymerization, and initiation) in free-radical polymerization (in a process called "grafting from"), or reacting an alkoxy silane chain-transfer agent during the homogeneous polymerization, then coupling it with the silica (in a process called

"grafting on"). This chain transfer agent may have one or three alkoxy sites: we chose the trialkoxy one, because we found that it was more strongly bonded to the support and more resistant to hydrolysis than the monoalkoxy.[11] The final purpose was to determine the best way to regularly cover the support with a definite chain length, either with a lot of short chains or with a few long chains. Optimization was attempted by control of the reaction parameters and investigation of the reaction medium. A number of physical methods were used to determine either the polymerization behavior or the basic phenomena in these heterogeneous media: mechanism, reactivity, free and masked species, steric effects, molecular weight control, etc.[12] Investigation of the porous structure was realized in the presence of solvents by inverse size exclusion chromatography as compared to classical methods.[13,14] Dramatic changes of pore size were obtained in aqueous or organic media for similar materials with different organization.

Then catalytic activity measurement was used as a tool for further choice of catalyst preparation. First the reaction was chosen. General guidelines were: Lewis or Bronsted catalysis, with a preference for a nonaqueous medium in order to avoid hydrolysis and bond scission between silica and polymer; moderate temperature to limit desulfonation; interest for industrial needs; and if possible, the existence of literature references in order to compare them with our results. To restrict the whole domain of possibilities, we fixed additional rules: different reaction mechanisms (addition, elimination, polar/nonpolar reagents or medium, different orders of reaction, etc.); use of different experimental devices; and moderate rate as a compromise between number of samples and number of experiments.

The three test reactions were acetal formation from cyclohexanone (CH) and ethylene glycol (EG) condensation, toluene alkylation with hexene, and *t*-butanol dehydration. Reference materials were the commercial Amberlyst 15 and *p*-toluene sulfonic acid (PTSA) as the molecular model. Catalytic activity was measured in relation to the structure and is the subject of the present article. The details of catalyst preparation are presented.

## EXPERIMENTAL

### Preparation of Materials

#### *Polymerization and Grafting*

Details for these processes are given in a previous study[11] and we recall here only the necessary in-

formation. Styrene (56 g) is polymerized for 6 h in toluene (233 g) with AIBN initiator (0.1 g) at 80°C under argon in the presence of trimethoxymercaptopropylsilane added continuously at a constant rate via a syringe from a 1 to 10% solution. After quenching the solution, alkoxy terminated polystyrene is recovered by evaporating the solution under a vacuum. The silica (Grace MP350, specific surface area 170 $m^2/g$, pore volume 1.7 mL/g, and average pore diameter 35 nm, bead diameter 0.5–1 mm) is dried 5 h at 200°C under argon. Five grams of silica are mixed with 10 g of functionalized polymer in toluene (250 mL) at 110°C for 24 h. Polymer grafted silica is filtered, washed, and dried under a vacuum at 80°C for 4 h. Grafted polystyrene is determined by weighing and by chemical and thermogravimetric analysis. Grafted polymer is recovered after dissolution of silica in fluorhydric acid (HF). Nongrafted polystyrene is recovered by precipitation with methanol and dried, as were intermediate polymers before grafting; all are characterized by size exclusion chromatography. Conditions are THF is the eluent, and three crosslinked polystyrene columns, a Waters R410 differential refractometer, and a data acquisition and treatment program with a laboratory-made device are used.

### *Sulfonation*

First the complex $SO_3$-triethylphosphate (TEP) is prepared by diluting $SO_3$ in dichloroethane (dried on a molecular sieve) to obtain a final concentration of 0.23 mol/L. The solution is cooled at 0 or −15°C because the reaction is exothermic. Then TEP is added slowly to attain a $SO_3$/TEP molar ratio of 1.5. Polystyrene grafted silica in suspension is added to this solution in an amount corresponding to a $SO_3$/aromatic rings molar ratio between 4 and 7. The temperature is allowed to increase up to 25°C and the reaction is run 2 h more. Finally an excess of TEP is added for neutralizing the solution (up to a $SO_3$/TEP ratio equal to 0.1). The silica is filtered. Then the solid is neutralized by a slow percolation of distilled water (1 L/g of silica). The absence of sulfate ions in the filtrate is tested by adding $BaCl_2$ and measuring the pH. Grafted silica is washed by methanol (50 mL/g) to make drying under a vacuum easier (0.01 mbar) at 60°C. Elemental analysis leads to the amount of sulfur. The sulfonation ratio is defined as the fraction of sulfonic aromatic rings.

**Table I  Sulfonation Conditions and Resulting Catalysts**

| Catalyst | SO$_3$/Ar Molar | GR (g/g sil) | Sulf. R (%) | Des. R (%) | SR$_f$ (%) | Capacity (mequiv/g) | CD (%) |
|---|---|---|---|---|---|---|---|
| 20 | 7 | 0.32 | 80 | 13 | 70 | 1.2 | 7.3 |
| 25 | 6 | 0.15 | 22 | 0 | 22 | 0.2 | |
| 26 | 5 | 0.20 | 88 | 33 | 59 | 0.9 | 3.3 |
| 29 | 6 | 0.11 | 68 | 26 | 50 | 0.4 | 15.2 |
| 30 | 4 | 0.37 | 65 | 16 | 55 | 1.3 | 3.7 |

GR, grafting ratio; sil, silanol; Sulf. R, % of sulfonation; Des. R, % of desulfonation; SR$_f$, final sulfonation ratio (fraction of sulfonated aromatic rings); CD, coverage density, is the fraction of functionalized silanol sites (%).

## Characterization

The analysis of Si and C allowed the determination of the amount of grafted polystyrene, as did thermogravimetry with a Ugine–Eyraud balance.[15] Grafting ratio is expressed in g polymer per g of silica. The number of grafted chains is calculated by dividing the weight of the polymer by its molecular mass (for instance $0.37 \times 6.10^{23}/12,200 = 18 \times 10^{18}$ grafted chains). Coverage density is calculated as the fraction of functionalized sites (for example, $18 \times 10^{18}/480 \times 10^{18} = 3.8\%$).

Solid-state cross polarization-magic angle spinning (CP-MAS) $^{29}$Si- and $^{13}$C-NMR analysis are performed with a Bruker AC 200 apparatus, equipped with a solid accessory, working at 39.76 and 50.3 MHz, respectively. Diffusion reflection FTIR is carried out on KBr pellets using a Nicolet 20 SX apparatus. These two methods ascertain the effective grafting of the coupling agent.

The solid morphology is characterized by mercury porosimetry up to a pressure of 400 MPa (which corresponds to 3.5-nm pore diameter) with an Autopore 9220 from Micromeritics. Accusorb 2100E from Micromeritics is used for the pore size distribution measurement.

Acid capacity of the final solid is measured by potentiometric titration after the reaction of the catalyst with a sodium hydroxide solution (added in excess). The unreacted NaOH is titrated by a known solution of HCl. Two equivalent points at pH 7 and 5 correspond to neutralization of hydroxy and carboxylate ions, respectively. The latter are avoided by working with water saturated with argon and by dilution under argon. Concentrated solutions allow a better reading at the equivalent point.
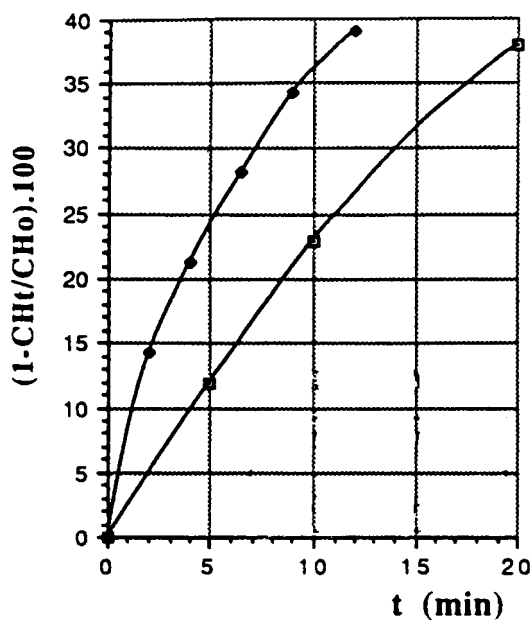


**Figure 1**  Conversion curve of cyclohexanone in the presence of catalyst 26 at H$^+$/CH ratio of (□) 0.016 and (◆) 0.030.
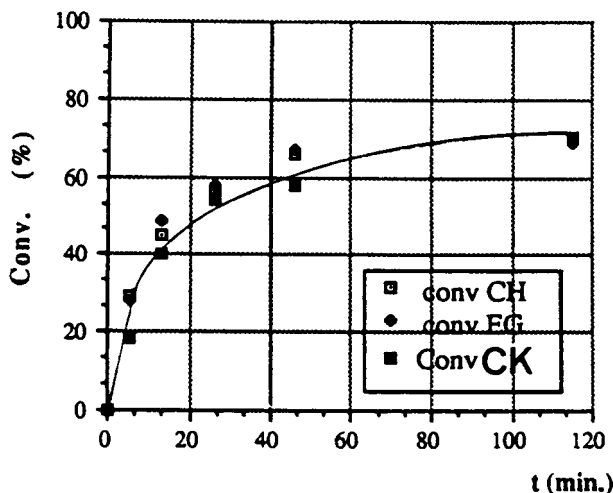


**Figure 2**  Conversion curves in EG, CH, and CK for cyclohexanone acetalization obtained in gas chromatography analysis from their peak areas.

**Table II   Acetalization between Cyclohexanone and Ethylene Glycol**

| Catalyst | eq H/CH $(10^6)$ | H (mequiv/L) | $C_f$ (%) | $t$ (min) | $10^3 R_0$ (mol/s/L) | $R_{sp}$ (mol/s/eq) |
|---|---|---|---|---|---|---|
| 20/1 | 11 | 3.2 | 76 | 180 | 0.60 | 0.19 |
| 20/2 | 22 | 6.4 | | | 0.82 | 0.13 |
| 20/3 | 33 | 9.9 | 70 | 115 | 1.60 | 0.16 |
| 20/4 | 97 | 25.6 | 70 | 93 | >2.40 | >0.09 |
| 26/1 | 17 | 4.6 | 69 | 228 | 1.09 | 0.23 |
| 26/2 | 31 | 8.7 | | | 2.51 | 0.29 |
| 29/1 | 9 | 2.6 | 69 | 190 | 1.25 | 0.48 |
| 29/2 | 12 | 3.5 | | | 1.25 | 0.36 |
| 30/1 | 8 | 2.3 | 68 | 1200 | 0.33 | 0.14 |
| 30/2 | 18 | 5.2 | 69 | 600 | 0.60 | 0.11 |
| 30/3 | 26 | 7.5 | 70 | 480 | 0.60 | 0.08 |
| 30/4 | 44 | 12.8 | | | 1.09 | 0.09 |
| AMB/1 | 54 | 15.7 | 69 | 241 | 0.82 | 0.05 |
| AMB/2 | 280 | 81.8 | 67 | 135 | >1.58 | >0.02 |
| PTSA/1 | 12 | 2.8 | 68 | 140 | >3.87 | 0>1.3 |
| PTSA/2 | 3 | 0.8 | | | 8.42 | 11 |

## Activity Measurement

### *Acetalization between CH and EG in Batch with GC Analysis*

A mixture of 5 g CH, 3.9 g EG, and 10 g dioxane in the presence of the chosen catalyst in various amounts is reacted under stirring at 40°C and in the presence of argon (to avoid water condensation). The CH/EG molar ratio is 0.8. Dioxane plays the role of solvent, internal reference, and diluent (to slow down this fast reaction). Parts of the solution are removed with the help of a sy-ringe and are frozen at liquid nitrogen temperature. They are analyzed by GC where ratios of the areas under the reagents, product, and reference peaks lead to the individual conversions.

The GC apparatus is from Delsi and is equipped with a Carbowax 20M column (1.5 mm × 1.7 m) under a nitrogen flow rate of 1 mL/min. The temperature ($T$) program is 2 min at 100°C, 2 min at 140°C, and 2 min at 180°C separated by $T$ increases at a rate of 25°C/min. Retention times are, respectively, 120, 242, 297, and 410 s for diox-ane, CH, cyclohexanone ketal (CK), and EG.
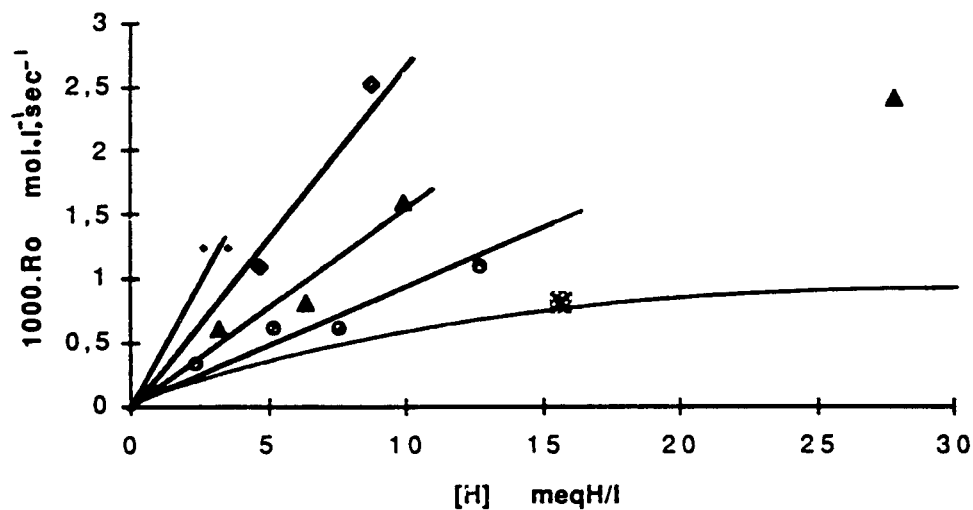


**Figure 3**   Initial rates according to the number of acid sites for various catalysts for cyclohexanone acetalization: (▲) 20; (◇) 26; (◆) 29; (●) 30; (×) Amberlyst 15.

**Table III   Acetalization between Cyclohexanone and Ethylene Glycol: Catalyst Characteristics and Reactivity**

| Catalyst | Capacity (mequiv/g) | $R_{sp}$ (mol/s/eq) | $10^5 R_m$ (mol/s/g) | $DP_n$ | $10^8$ CR (mol/m$^2$) |
|---|---|---|---|---|---|
| 30 | 1.3 | 0.11 | 15 | 122 | 13 |
| 26 | 0.9 | 0.25 | 18 | 73 | 13 |
| 20 | 1.2 | 0.14 | 15 | 54 | 21 |
| 29 | 0.6 | 0.44 | 24 | 9 | 43 |
| Amb. | 4.7 | 0.05 | 24 | | |
| PTSA | 5.8 | 11.00 | 6400 | | |

Amb., Amberlyst 15.

### Toluene Alkylation by 1-Hexene

Attempts are made in the batch or in a tubular reactor with GC analysis.

Toluene and 1-hexene are dried under a 3-Å molecular sieve and the catalyst is dried under vacuum for 3 h at 60°C. In the batch a mixture of toluene, catalyst, and $n$-octane (as internal reference) is put in a glass vessel equipped with a refrigerator tube and argon inlet. After adjusting at the desired temperature, 1-hexene is added under stirring (corresponding to $t = 0$). The conversion is determined on cooled samples by GC from the ratio of the peak areas of 1-hexene and $n$-octane. The initial 1-hexene/toluene molar ratio is 0.26.

For the fixed-bed experiments, the reactor is a stainless steel column ($25 \times 0.8$ cm/capped, with a semicapillary tube) dipped in an ice bath. The column is in a heating mantle with temperature regulation. The reagents and standard are in a cylinder maintained at 22°C; they are moved to the reactor by a liquid chromatograph pump at a 1.1 mL/min flow rate. The molar composition is 40/16/14, respectively, for toluene, 1-hexene, and $n$-octane. The volume reactor is 12.6 cm$^3$, so the average contact time is 126 min.

GC analysis is performed on a capillary column at a nitrogen flow rate of 0.4 mL/min, starting at 30°C for 3 min and increasing the temperature to 80°C for 2 min at a rate of 25°C/min. The retention times are 18, 34, 96, and 430 s, respectively, for 1-hexene, $n$-octane, toluene, and monoalkylate.

### t-Butanol Dehydration with Pressure Sensor Gauge Analysis

A glass flask (270 mL) is equipped with a pressure sensor gauge, a vessel containing the reagent ($t$-butanol in the presence of octane as internal reference, volume ratio 5/1), and a vacuum/argon circuit. The chemicals are dried over a molecular sieve and the catalyst is dried 3 h under vacuum at 60°C. The material is dried in an oven. Everything is handled under argon. The reactor is in a
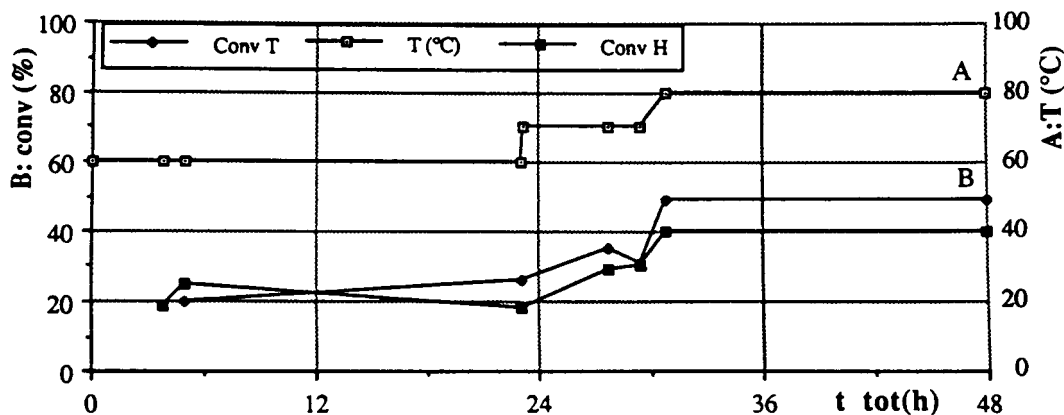


**Figure 4**   Percent conversion [curves B, ( ♦ ) toluene, ( ■ ) hexene] in toluene alkylation vs. time at three temperatures (60, 70, 80°C, curve A) in the presence of catalyst 26.
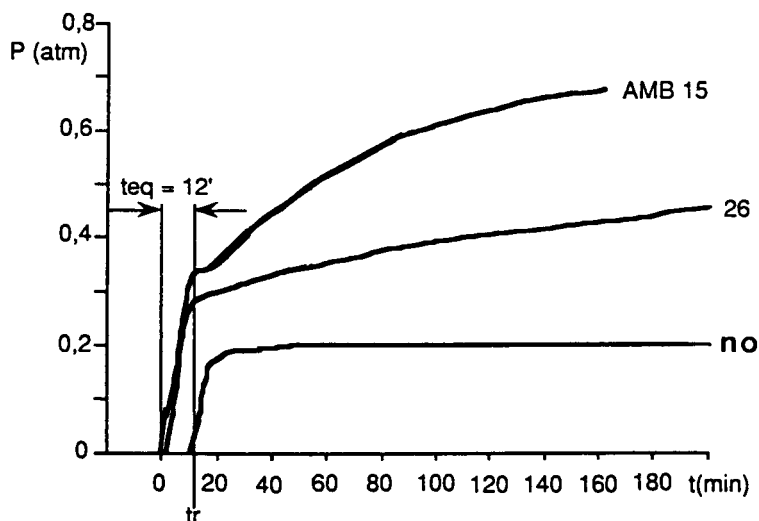
**Figure 5** Pressure evolution with time for two catalysts (26 and Amberlyst 15) and without catalyst (added time 12 min) for *t*-butanol dehydration (teq, equilibrium time; tr, initial time).

thermostated bath at 65°C. It contains the catalyst to which 6 mL of solution is added. Thermodynamic equilibrium is obtained for 20–25% conversion. The final pressure is between 0.5 and 1.3 bar, depending on the catalyst. In the absence of a catalyst, for a blank experiment, vapor pressure at saturation is 0.2 bar. Solubility of isobutene in butanol and in the butanol/octane mixture at a volume ratio of 5/1 is measured by a weighting method; it is 5.7 mg/g solution.

Isothermal GC analysis is performed at 100°C on a packed column (SE 30, 4.8 m × 1.5 mm) at a nitrogen flow rate of 0.7 mL/min. Retention times are 36, 52, and 172 s, respectively, for isobutene, *t*-butanol, and *n*-octane.

## RESULTS AND DISCUSSION

A description of the catalysts may be found in the tables, mainly Table I. Let us say that chain length varies from 9 to 122 and the polymolecularity index is about 2 for the grafted polystyrene. The final extent of sulfonation degree is about 60% because the sulfonation process is accompanied by scission of a part of the polymer bonds to silica. The choice of the trifunctional thiol limits this scission to less than 25% instead of more than 60% with the monofunctional grafting agent.[15] The capacity lies between 0.4 and 1.3 meq/g. The pore volume is decreased to 1.1 mL/g and the area to 120 $m^2$/g, which correspond, respectively, to a 35 and 30% decrease for 140 mg polymer/g. The pore volume diminution is larger than that expected from the volume of a solid polymer. This may be explained by a large chain expansion and by partial blocking of pores. Experiments in liquid media by inverse size exclusion chromatography indicate that a dramatic change of pore size is obtained in aqueous or organic media for similar materials with different organization (micro-

**Table IV  *t*-Butanol Dehydration: Conditions and Reactivity**

| Catalyst | Grams | $H^+$ (mol/L) | $10^4\ dP/dt$ (bar/s) | $10^4\ R$ (mol/L/s) | $10^4\ R_{sp}$ (mol/s/eq) |
|---|---|---|---|---|---|
| Amb.[a] | 0.24 | 0.06 | 0.48 | 0.4 | 5.7 |
| Amb. | 0.16 | 0.13 | 1.37 | 3.0 | 24 |
| Amb.[b] | 0.16 | 0.13 | 2.18 | 4.8 | 38 |
| 26 | 0.52 | 0.08 | 0.23 | 0.5 | 6.5 |
| 29 | 0.80 | 0.08 | 0.40 | 0.9 | 11.0 |

Amb., Amberlyst 15. $T = 65$°C and $V = 6$ mL.
[a] $T = 50$°C and $V = 18$ mL.
[b] With added molecular sieve.

**Table V  *t*-Butanol Dehydration: Reactivity from Pressure and Chromatography Analysis**

| Catalyst | $P_f$ (bar) | Conv. (%) | Conv. GC (%) |
|---|---|---|---|
| Amb. | 1.20 | 18 | 20 |
| 26 | 0.63 | 20 | 10 |
| 29 | 0.70 | 22 | 25 |

Amb., Amberlyst 15.

structure), in agreement with the swelling hypothesis and effect of hydrophilic sites.[14]

## Acetalization between CH and EG in Batch

The first test concerns two polar reagents in a condensation process with water elimination. As indicated in the introduction, this reaction obeys several criteria such as the high activity of acid catalysts at room temperature as well as the ease of reagents and products characterization. The products are of interest in sugar chemistry, the pharmaceutical industry, and protection or isolation of aldehydes and ketones. Literature catalysts are Bronsted acid HCl, PTSA, sulfonic resins, and Lewis acids ($TiCl_4$, $FeCl_3$, $ZnCl_2$). The mechanism involves a hemiacetal intermediate that produces an oxonium ion after dehydration; the acetal is destroyed in an aqueous medium and the steps are reversible. The kinetics results are not shown. The reaction is complete if water is removed.[16]

Our batch experiments are made in the presence of different amounts of several catalysts with different capacities. Activity is characterized by the initial rate, the initial specific rate (for 1 meq/g).[1] The final conversion at the thermodynamic equilibrium is about 70% (in all attempts, PTSA included). The reference materials are PTSA and Amberlyst 15. Blank experiments are made on untreated silica and in the absence of catalyst, where no activity is found in both cases.

Figure 1 presents conversion curves for two amounts of catalyst 26. The rate increases with catalyst concentration; complementary experiments indicate an approximate first-order law. The activity per acid site is excellent because the reagent/site ratio is about $10^5$. Selectivity is excellent because conversion obtained from reagent disappearance or product formation by GC analysis is the same (Fig. 2). Moreover, no secondary product is detected by GC analysis. Table II sum-

marizes several results that indicate some proportionality between the initial rate and catalyst amount, activity for silica catalysts higher than for Amberlyst but lower than for PTSA, and different values of the specific rates according to the catalysts. The higher activity of a strong acid in the molecular state is normal, as expected, for a free and small species. The higher activity of the silica catalyst may be explained by its pellicular structure (as compared to the porous one of Amberlyst) where the sites are located inside the whole volume, so that rate is diffusion controlled. Moreover, silica has a higher compatibility with the polar reagents than the styrenic network, as demonstrated by UV-visible fluorescence.[17,18] In a good solvent, grafted polymer adopts a fully elongated configuration and is expected to be more accessible than a crosslinked polymer. In a poor solvent the hydrophilic chain is expected to interact preferentially with the hydrophilic silica surface. Hydrogen bonds are formed between sulfonic groups and polar silanols. As a consequence, activity is decreased. Figure 3 illustrates the effects of catalyst amount and catalyst nature. One feature is expected: a general and constant increase of rate is observed with an increase of acidity. But different curves are obtained, according to the catalyst structure. The effect of catalyst structure is also illustrated in Table III. A maximal activity per acid site ($R_{sp}$) is found for the higher coverage ratio combined with the lower chain length. This maximum is also found by considering the activity per gram of catalyst ($R_0$), where the more active catalyst has the lower capacity. Nevertheless, a catalyst with a capacity of 0.2 and used at a low amount is rather inactive. The activity is corre-
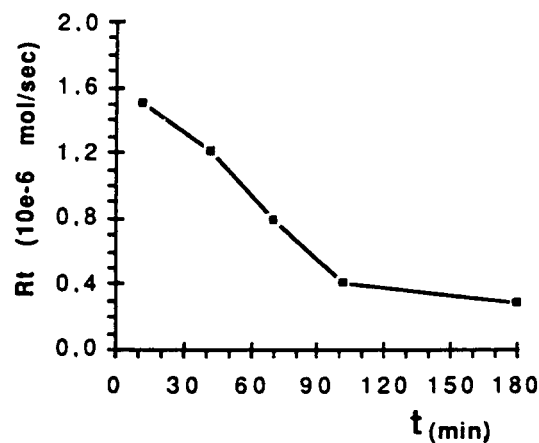


**Figure 6**  Decrease of instantaneous rate in the presence of Amberlyst 15 for *t*-butanol dehydration.

lated with accessible sites on the short chains, which cover an optimal part of the surface.

### Toluene Alkylation by 1-Hexene

In this example two nonpolar molecules are of concern and water is absent at the difference of the previous reaction between polar reagents in a polar solvent with water production. Alkylation reactions are widely used in the industry for detergents synthesis and the preparation of basic molecules such as styrene or phenols. Catalysts are Lewis and Bronsted acids supported on metal oxides, clays, silica-alumina, or silica-magnesia. Dimers and oligomers formation are frequent side reactions. Benzene alkylation with hexene in the presence of sulfonic resins has a large increase in reactivity with an increase of sulfonated rings fraction, which indicates some cooperative effect.[17-19]

The catalyst has good stability at each temperature in a continuous 48-h test starting at 60°C and going on at 70 and 80°C; hexene conversion increases with $T$ from 20 to 30 and 40% (Fig. 4). A comparison of activity with Amberlyst 15 shows a similar value (4 vs. $10 \times 10^{-4}$ mol/s/eq) that is relatively low compared to that of AlCl$_3$ for instance (0.5 mol/s/eq).[15] Selectivity in monoalkylation of the present catalyst is better than that of supported Lewis acids; in this case di- and trialkylates are formed in large amounts whereas they appear as very small peaks only after concentration of the solution from our tests either with silica or Amberlyst.

In spite of their excellent stability and selectivity, the low activity of these catalysts does not allow a comparative study of the function of the morphology.

### *t*-Butanol Dehydration with Pressure Sensor Gauge Analysis

Many studies are relative to alcohol's dehydration in the presence of acids such as Amberlyst 15 or Dowex 50M.[20-22] Sulfonic acids are also catalysts for the reverse reaction of isobutene or isomerization and oligomerization. Cooperative effects are also evident, so that activity is sharply increased (10 times) when the aromatic sulfonic group fraction is high. Activity is divided by 2 at 20% neutralization and by 30 at 70% neutralization. Water has a strong effect: the rate is divided by 3 for a water molar fraction of 0.1, so that it must be eliminated (at reflux or by azeotrope formation

with benzene) for continuous processes.[22] Possible secondary reactions (reverse reaction and oligomerization) occur infrequently because isobutene concentration is very low in the liquid phase.

Typical pressure curves related to conversion are presented in Figure 5. The first increase is due to equilibrium establishment between the liquid and gas phases when butanol is added in the reactor previously under a vacuum. Equilibrium is obtained after 12 min when measured in the absence of a reaction of no catalyst or pure silica. This time is chosen to express initial conditions. By assuming the validity of the perfect gas law, a pressure increase is transformed in a reaction rate in moles per liter per second and specific rate in moles per second per equivalent. Our catalysts are compared to Amberlyst 15 in the same range of acid sites number. Table IV summarizes the results. Table V indicates final conversions obtained by this method and calculated by GC at the end of the reaction; they are in good agreement.

The method leads to reproducible values. They are of the same order as that of Amberlyst. Yet, that value (in octane) is inferior to the value calculated from the results of Gates et al.[21] that is measured without diluent at the initial time and at a different temperature. (For comparison we extrapolated from their result at 80°C by using their value of activation energy.) Finally, we measure a rapid decrease of the reaction rate with time corresponding to inhibition by water (Fig. 6). By adding a molecular sieve, we obtain a 50% rate increase, which corresponds to a partial water transfer from resin to the drying agent.

With some of our weakly sulfonated catalysts (0.2 meq), no conversion is observed. For catalysts of different capacity but used at the same acid concentration, the activity in this test corresponds to the previous observations for the first test; for example, catalyst 29 is better than catalyst 26.

## CONCLUSION

Defined materials with controlled morphology were synthesized to determine the factors leading to the best activity. They were various chain length alkoxy terminated polystyrenes that were reacted with porous silica in different amounts. An increase of reactivity was measured for some reactions as compared to that of ion-exchange resins. For others, the activity was lower. The reason lies in the compatibility between the support and

reagents: it was poor for toluene alkylation and good for oxygenated reagents (ketones, alcohols). The reactivity and stability depended on the presence and elimination of the water. Selectivity was excellent. The second important result was that a high number of short chains was better than a low number of long chains at a given polymer to silica ratio. Better accessibility (pellicular structure in the whole volume), better coverage ratio (percentage of functionalized silanols sites), and chain flexibility (instead of a crosslinked structure) combined with a convenient adjusted environment (hydrophilicity) explained behavior differences from that of improved ion-exchange catalysts.

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