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Ketalization of Ketones to 1,3-Dioxolanes and Concurring Self-Aldolization Catalyzed by an Amorphous, Hydrophilic SiO_2-SO_3H Catalyst under Microwave Irradiation

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The amorphous, mesoporous SiO_2-SO_3H catalyst with a surface area of 115 $m^2\,g^{-1}$ and 1.32 mmol H^+ *per* g was very efficient for the protonation of ketones on a 10% (m/m) basis, and the catalyst-bound intermediates can be trapped by polyalcohols to produce ketals in high yields or suffer aldol condensations within minutes under low-power microwave irradiation. The same catalyst can easily reverse the ketalization reaction.

Keywords: protonated ketones, self-aldolization, ketalization, ketal hydrolysis, sulfonated silica

Introduction

Sulfuric acid can be considered to be the standard acid for all organic reactions that are catalyzed by strong Brønsted-Lowry acids, but its anti-Green-Chemistry nature impairs its widespread use: its residues are highly acidic and its corrosiveness is widely avoided. On the other hand, solid acids such as sulfonated silicas have been shown to bear a sufficient number of acidic sites, with little tendency for lixiviation,[1] to make them versatile candidates for the replacement of the homogeneous sulfuric acid. The SiO_2-SO_3H catalysts can be prepared in several ways. Examples range from the simple addition of H_2SO_4 to slurries of silica and ether[2,3] or the treatment of silica with chlorosulfonic acid[4] to more complex synthesis of mesoporous materials where the sulfonic groups are separated from the surface of the silica by carbon chains.[5] This method is also a form of diminishing the hydrophilicity of the catalyst.[6] We recently developed a mesoporous, sulfonated silica as a Brønsted acid, whose high hydrophilicity made it ideal for the catalysis of water-forming, proton-assisted organic transformations, such as the formation of ethers from alcohols and the esterification of acids with alcohols, equations 1 and 2.[7] SiO_2-SO_3H[8] and SiO_2-$(CH_2)_3$-SO_3H[6] have been reported to catalyze ketal formation from ketones and ethylene glycol, which is also a water-forming reaction involving the equilibrium shown in equation 3.

$$2\,\text{R-OH} \underset{[\text{SiO}_2\text{-SO}_3\text{H}]}{\rightleftharpoons} \text{H}_2\text{O} + \text{R-O-R} \tag{1}$$

$$\text{RCO}_2\text{H} + \text{R'-OH} \underset{[\text{SiO}_2\text{-SO}_3\text{H}]}{\rightleftharpoons} \text{H}_2\text{O} + \text{RCO}_2\text{R'} \tag{2}$$

The carbonyl groups of aldehydes and ketones are quite reactive and must be protected if the compounds bearing such groups are to be subjected to chemical transformations where the aldehyde or ketone functions

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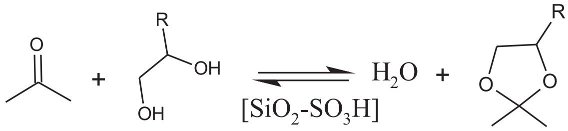
might be destroyed. Usually this protection is accomplished by the reaction of the carbonyl compound with ethylene glycol in the presence of an acid catalyst.[9] The products are usually referred to as an acetal if prepared from an aldehyde, or ketal, if formed from a ketone. They contain the backbone of the 5-membered 1-3-dioxolane ring. This ring must be hydrolyzed in the presence of an acid catalyst, to liberate the ethylene glycol and the carbonyl compound after the desired transformation. Apart from the great importance of such protection and deprotection reactions, some ketals are useful themselves, such as those from glycerol; these ketals can be used as precursors for the synthesis of monoglycerides, as food emulsifiers,[10] as chiral building blocks in organic synthesis[11] or as fuel additives for biodiesel.[12] 1,3-Dioxolanes have also been shown to exhibit antimicrobial activity against Gram-positive and Gram-negative bacteria and can be used as antiseptics for sterilization of working surfaces and instruments.[13] The six-membered ring ketals, or m-dioxanes, are also of interest for the pharmacy and fuel industries.[14] We now report that reactions such as equation 3 can be greatly enhanced by microwave irradiation using our hydrophilic catalyst and that the procedure can be extended to other polyols such as trimethylol propane, neopentyl glycol and crude glycerol. In the absence of alcohols, the ketones tested were rapidly protonated to produce aldol condensates (equation 4), except for benzophenone.



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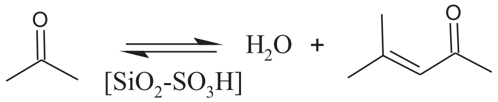


(4)

Experimental

Raw materials

The alcohols ethylene glycol, 2-ethyl-2-hydroxymethylpropane-1,2-diol (trimethylol propane), and 2,2-dimethylpropane-1,3-diol (neopentyl glycol) and the ketones propanone, cyclohexanone, acetophenone, 4-methylacetophenone and benzophenone were used as purchased; crude glycerol was obtained from the transesterification of waste cooking oil with methanol.

Instrumentation

The infrared spectra of solid samples were recorded as KBr pellets in the 4000-400 cm^{-1} range on a Varian 640 spectrophotometer operating in the FT mode. X-ray diffraction (XRD) patterns were collected on a Rigaku diffractometer at 30 kV and 20 mA using CuKα radiation. Differential thermal analysis (DTA) was carried out using a PerkinElmer 1700 analyzer. Ketal contents and yields were determined with a gas chromatography mass spectrometer GC-MS-QP 2010 Shimadzu equipped with an AOC 5000 Auto Injector and a 30 m Agilent J&W GC DB-5 MS column. Direct insertion spectra were measured at 70 eV. Quantitative analyses were performed on a Shimadzu GC-2010 gas chromatograph equipped with a flame ionization detector (FID). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance 400 and Avance 500 spectrometers. All the reactions were performed under atmospheric pressure, using microwave irradiation and monitored by thin layer chromatography (TLC) with Silica Gel 60 F254 on aluminum. The chromatograms were visualized by UV or by using an ethanolic vanillin developing agent. Silica gel (Merck 230-400 mesh) was used for purification of products by flash column chromatography using hexane/ethyl acetate (8:2) as eluent.

Preparation of the silica gel and the sulfonated silica, SiO_2-SO_3H[7]

A mixture of 300.0 g of sand and 600.0 g of sodium carbonate were homogenized and transferred to porcelain crucibles, which were heated at 850 °C for 4 h. The hot solid mixtures were transferred to a glass filter frit and washed with 600-900 mL of boiling water. The filtered solution was acidified to pH = 1 with hydrochloric acid, the white precipitate was filtered, and dried at 400 ºC. The resulting silica was passed through a 24 mesh sieve for standardization. 10.0 g of the prepared silica was mixed with 10.0 mL of H_2SO_4 and stirred at room temperature for 12 h, filtered and dried at 150 °C for 4 h, cooled and stored in a desiccator. The acid strength of 1.32 mmol of H$^+$ *per* gram of catalyst was determined by potentiometric titration.

Typical procedures

All the reactions were irradiated in an unmodified microwave (MW) oven (900 GHz)/360 W using an open 125 mL two-necked round bottom flask and were accompanied by TLC or GC-MS. Typically, the amount of catalyst was weighed directly into the flask, and the desired quantity of the ketone and alcohol, where applicable, were added, the mixture quickly mixed by shaking and, immediately, irradiated. The silica catalyst does not allow the final temperature of the slurries to exceed 73 ºC (see also reference 7). To each of the cooled vessels from the reactions, 30.0 mL of diethyl ether was added, and the mixture was filtered. The organic extracts were washed with 10.0 mL of saturated $NaHCO_3$, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residues were purified on chromatographic columns using hexane/ethyl acetate 8:2 as eluent (with the exception of solketal, which was distilled) to furnish the pure products as colorless oils. For the synthesis of ketals, the amounts of ketone (1.0 mmol) and alcohol (5.0 mmol) were maintained throughout; the amount of catalyst used in each run was adjusted to maintain a constant 10% mass-to-mass ratio to the ketone, and the reactions were irradiated for 2 to 7 min. The ketals were identified by GC-MS, electrospray ionization time-of-flight (ESI-TOF) mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy. For the synthesis of α,β-unsaturated ketones, the amount of catalyst was adjusted to 10% (m/m) relative to 1.0 mmol of the ketones (acetone, methyl ethyl ketone, cyclohexanone, acetophenone and *p*-methylacetophenone). All the reaction media were irradiated for 6 min, except for acetone, whose reaction was performed in a conventional heating mantle (12 h of reflux). The α,β-unsaturated ketones were identified by GC-MS and ^{1}H and ^{13}C NMR spectroscopy.

All the reactions were performed under atmospheric pressure, using a heating mantle and, except for acetone, microwave irradiation, and monitored by TLC with Silica Gel 60 F254 on aluminum. The chromatograms were visualized by UV or by using an ethanolic vanillin developing agent. Silica gel (Merck 230-400 mesh) was used for purification of products by flash column chromatography using hexane/ethyl acetate (9:1) as eluent.

For the hydrolysis of the ketals, the amount of catalyst was adjusted to 20% (m/m) in relation to the ketal (1.00 mmol), and an excess of water (10.00 mL) was added to minimize the auto condensation reactions of the ketone products. After irradiating 2 min at 360 W, the mixture was cooled, mixed with 20.00 mL of ethyl ether and filtered. The organic mixture was extracted with an aqueous NaCl solution, dried with $MgSO_4$ and concentrated; GC-MS analyses of these extracts confirmed 94-98% yields. The alcohols and ketones were finally separated by column chromatography using a mixture of hexane/ethyl acetate 8:2 as eluent. Ethylene glycol and 20% (m/m) SiO_2-SO_3H was irradiated for 6 min to produce diethylene glycol in 96% yield after the same chromatographic purification procedure.

Results and Discussion

Silica gel and catalyst, SiO_2-SO_3H, characterization

The non-crystalline natures of the silica gel and of the SiO_2-SO_3H catalyst were confirmed by XRD, which presented broad peaks centered at $2\theta = 23°$,[7] Figure 1.

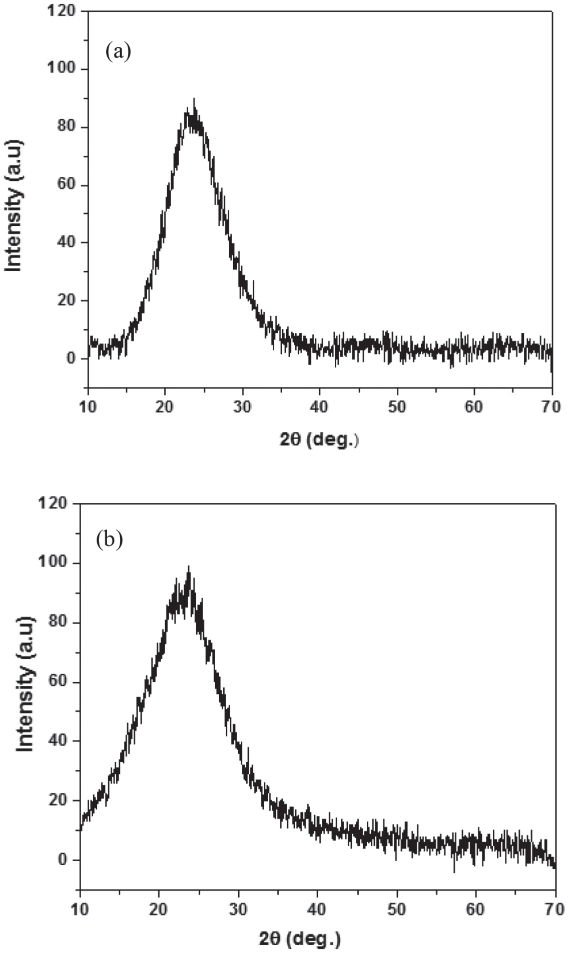


Figure 1. X-ray powder pattern of (a) precipitated silica gel and (b) SiO_2-SO_3H catalyst.

The infrared spectrum of the silica (Figure 2a) is also representative of an amorphous silica gel.[7] The characteristic absorption bands around 3400 and 1630 cm^{-1} are associated with the stretching and bending modes of molecular water, whereas the shoulder at 3200 cm^{-1} and the weak absorption at 960 cm^{-1} are related to the –OH and Si–OH vibrations of the silica silanol groups.[7] The bands at 1090 cm^{-1} and the associated shoulder at 1190 cm^{-1} are characteristic of the asymmetric stretching modes of the Si–O–Si bonds.[7] The absorption at 800 cm^{-1} of the ring-structured tetrahedral SiO_4 (Si–O–Si symmetric stretchings), the Si–O–Si bending vibrations at 470 cm^{-1} and the overtones typical of the

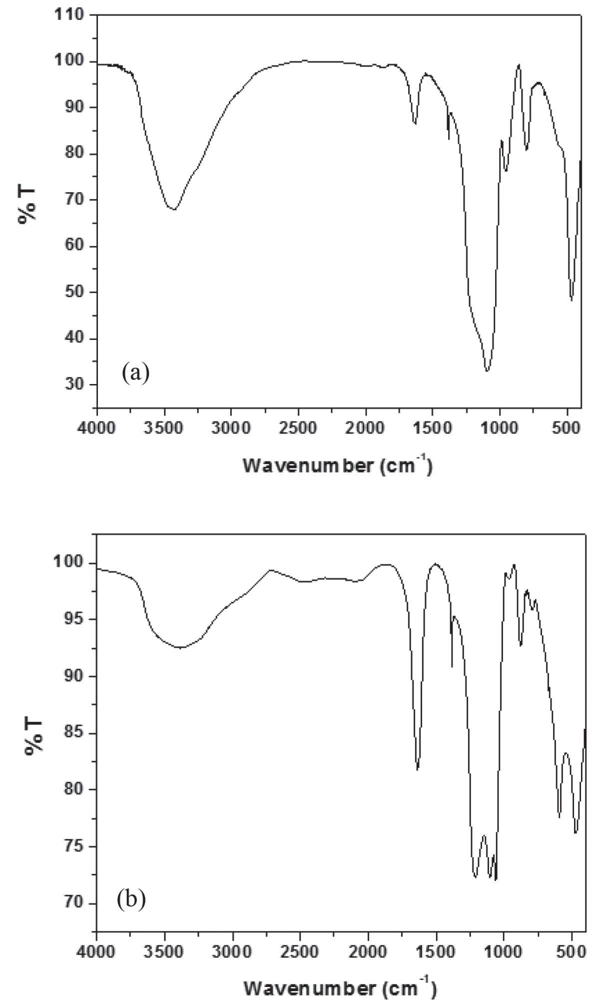


Figure 2. FTIR spectra of the (a) silica gel and (b) SiO_2-SO_3H.

amorphous silicas in the region of 1800-1900 cm^{-1} complete the spectrum of the gel.[7] The infrared (IR) spectrum of the SiO_2-SO_3H catalyst (Figure 2b) presented remarkable differences. For instance, the H_2O bands at 3400 cm^{-1} are much broader, with additional intramolecular hydrogen bond features at 2900-2100 cm^{-1} and the concomitant increase of the H_2O bending at 1637 cm^{-1}. These changes certainly reflect the accommodation of additional water molecules via hydrogen bonds to the –SiOH and –O–SO_3H groups of the SiO_2-SO_3H. The splitting of the absorptions from 1210 to 1040 cm^{-1} in the spectrum of the catalyst, which indicates a profound modification of the overall surface structure of the Si–O–Si original arrangement, are also reflected in the further weakening of the Si–OH band at 960 cm^{-1}. The contributions of the –O–SO_3H groups to the absorptions of the IR spectrum of the catalyst are ambiguous because of the close proximity of the atomic weights of tetrahedral silicon and sulfur. However, one might assume that the enhancement of the Si–O–Si longitudinal-transverse optical vibration (LO) absorption at 1210 cm^{-1} and the transversal optical (TO) rocking of the Si–O–Si bonds at 592 cm^{-1} may be due to the presence of the –OSO_3H groups of the catalyst.[7]

The striking differences between the original silica and the SiO_2-SO_3H catalyst is also evident from the field emission scanning electron microscopy (FE-SEM) images shown in Figures 3 (silica) and 4 (catalyst) at different magnifications. It is apparent that the even distribution of the particles of the silica, which are responsible for its large surface area, tend to form aggregates upon sulfonation. The aggregates formed upon sulfonation are well separated by macropores several nanometers in diameter.

Textural parameters of materials were studied by N_2 adsorption/desorption isotherms, Figure 5, that showed a type IV behavior with H1 hysteresis, typical of mesoporous materials, which are related to pores with a constant transversal section.[7] After silica surface modification with –SO_3H groups, there was a decrease in surface area of 507 to 115 m^2 g^{-1}, and a volume of pores decrease of 0.78 to 0.38 cm^3 g^{-1}.

The thermal behaviors of the new silica gel and catalyst were evaluated. The thermogravimetric analysis

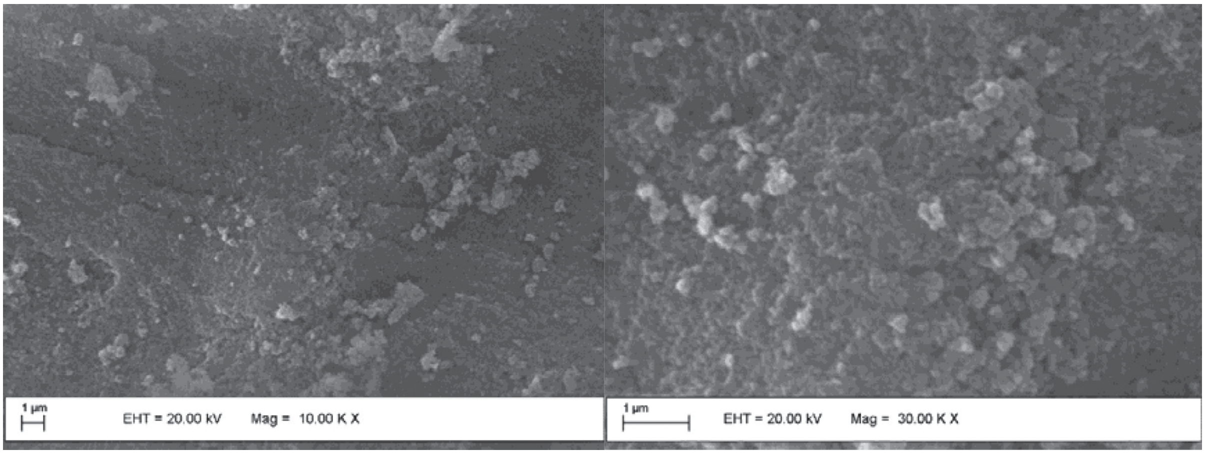


Figure 3. FE-SEM images of the amorphous silica gel.

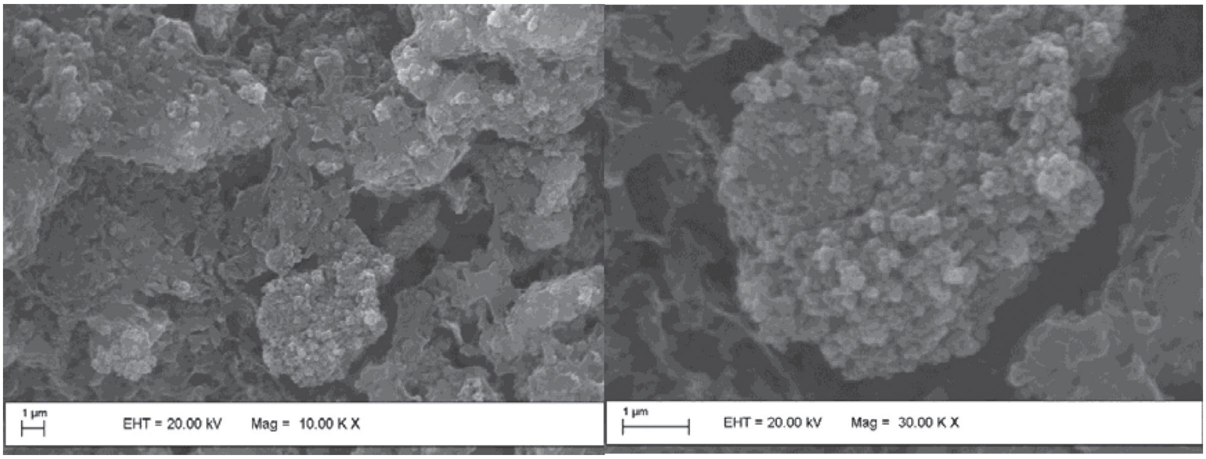


Figure 4. FE-SEM images of the SiO_2-SO_3H.

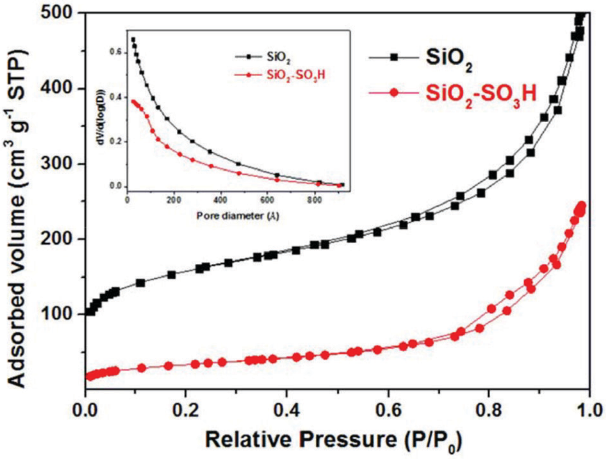


Figure 5. N_2 adsorption/desorption isotherms and (inset) Barrett-Joyner-Halenda (BJH) method to pore size distributions for pure silica (SiO_2) (black squares) before modifications and SiO_2-SO_3H (red squares).

(TGA/DTG/DTA) curves for silica and catalyst, respectively, are presented in Figure 6.

The decomposition of silica gel in a synthetic air atmosphere takes place in one step. This step, from room temperature to 149.71 ºC, is related to the endothermic elimination of water molecules and the formation of anhydrous silica. The decomposition of the catalyst takes place in two stages. The first step, from room temperature to 169.39 ºC, is also related to the endothermic elimination of water molecules and the formation of anhydrous catalyst; the second step, up to 240 °C, corresponds to the endothermic loss of sulfur trioxide.

General remarks

Of particular interest for this work, both SiO_2-SO_3H[8] and SiO_2-CH_2-CH_2-CH_2-SO_3H[6] have been used with success for ketalization reactions using conventional heating with reaction times extending up to 12 h. An example involves the preparation of the cyclohexanone ketal in 90% yield using toluene as the solvent and heating at reflux temperature for 3 h.[6] The same reaction was performed using SiO_2-SO_3H as the catalyst in the absence of solvent under low microwave irradiation power (360 W). The temperature of the slurry did not exceed 73 ºC, and a 99.9% yield was obtained in only 2 min (entry 1 in Table 1).

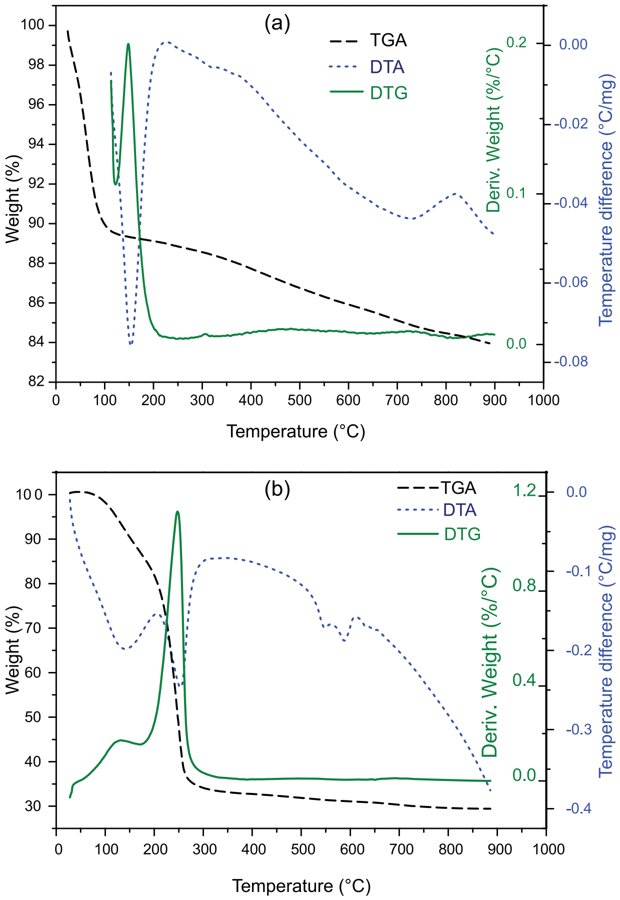


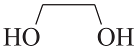
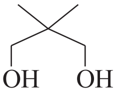
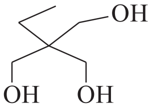
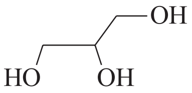
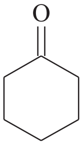
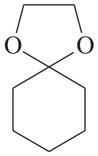
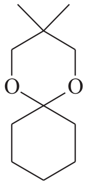
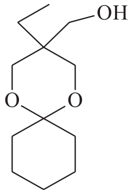
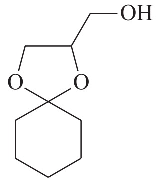
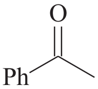
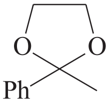
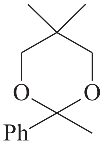
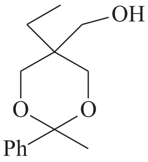
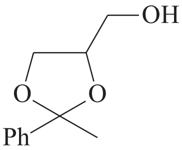
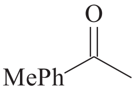
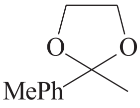
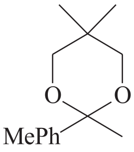
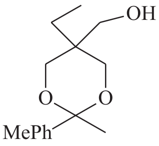
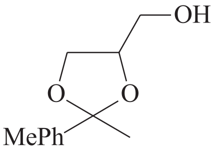
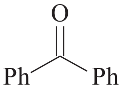
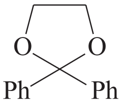
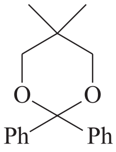
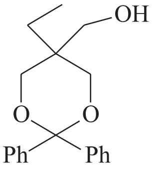
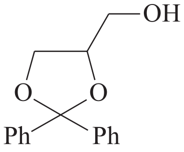
Figure 6. TGA/DTG/DTA curves of (a) new silica gel and (b) catalyst in a synthetic air atmosphere (25 to 900 ºC).

However, these experimental conditions yielded only about 50% of the acetophenone ketal (entry 5, Table 1), against 93% yield (10 h reflux) using the propyl-modified catalyst.[6]

The formation of six-membered ketals seems to be favored over the formation of 1-3-dioxolanes, in particular those of the seemingly less reactive benzophenone (entries 14 and 15, Table 1). No formation of the six-membered isomers of the ketals involving glycerol, which did fail to react with benzophenone under our solvent-free condition, was observed. Amongst those glycerol ketals shown in Table 1, the ciclohexanone derivative had already been obtained in 90% yield by high power microwave irradiation (600 W, 140 ºC, 15 min).[15] All the ketalization reactions in Table 1 can be reversed by the addition of water to the ketals in the presence of SiO_2-SO_3H, as has already been pointed out by Rajput *et al.*;[2] under microwave irradiation, this reaction takes only 2 min to complete (see Experimental section).

During our attempts to carry on the ketalization reactions using conventional heating, it became clear that concurrent reactions occurred using our SiO_2-SO_3H catalyst, namely, etherification and aldol condensation.

Table 1. Ketalization of ketones with polyalcohols using SiO_2-SO_3H catalyst and MW irradiation. Alcohol to ketone ratio 5:1, 10% (m/m) catalyst

				
	(**1**)  99.9% 2 min	(**2**)  99.0% 4 min	(**3**)  65.6% 7 min	(**4**)  70.5% 5 min
	(**5**)  50.5% 2 min	(**6**)  93.6% 5 min	(**7**)  66.3% 3 min	(**8**)  58.9% 2 min
	(**9**)  49.7% 2 min	(**10**)  75.1% 5 min	(**11**)  63.6% 3 min	(**12**)  55.6% 5 min
	(**13**)  28.9% 5 min	(**14**)  49.3% 5 min	(**15**)  53.5% 8 min	(**16**)  0% 8 min

Because we had already noted the strong tendency of our catalyst to catalyze the formation of ethers from benzyl alcohol,[7] we decided to perform the detailed study of the interaction of cyclohexanone and ethylene glycol at different ketone to alcohol ratios and different catalyst loads using 360 W MW irradiation. The load of the catalyst, from 7 to 20% (m/m), had only a minor effect on the reaction product distribution, which was very dependent on the alcohol to ketone ratio. Figure 7 resumes these findings.

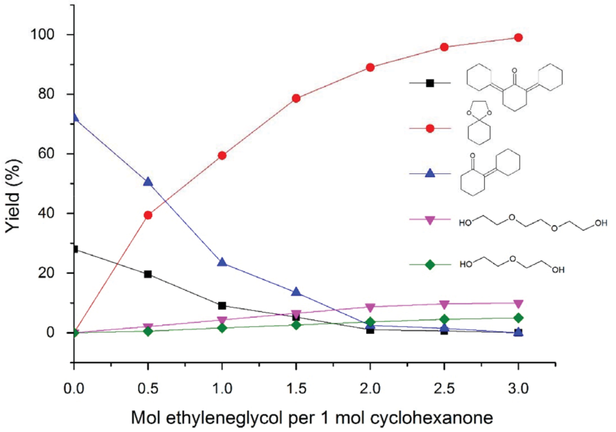


Figure 7. Product distribution of the reaction of 1 mol equiv. of cyclohexanone to 0-3 mol equiv. ethylene glycol, 10% (m/m) of catalyst to ketone; 2 min MW irradiation at 360 W; final temperature ca. 70 ºC.

Figure 7 shows that cyclohexanone readily self-condenses in the presence of the sulfonated catalyst, but this reaction becomes negligible at 2:1 or higher ratios of glycol to ketone. However, at these higher ratios, the condensation of the alcohol becomes important. In the absence of a ketone, ethylene glycol is converted to bis-ethylene glycol (**17**) in 96% yield (see Experimental section). It must be noted that the catalyst could be used three times, with very little loss in activity (under microwave irradiation conditions). Table 2 summarizes the self-condensation of the ketones.

Proposed mechanism

While examining the esterification of benzoic acid with benzyl alcohol, we observed that, at higher concentrations, the catalyst SiO_2-SO_3H had an increased affinity for organic alcohols *versus* organic acids, and we proposed[5] the existence of a catalyst-bound species of the type $[Bz–OH_2]^{+**}$ (Bz-OH = benzyl alcohol; ** = catalyst bound species) as important intermediates, so that reactions such as equations 5 and 6 could result in the exclusive formation of dibenzyl ether from a mixture of benzyl alcohol and benzoic acid.[7]

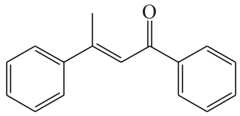
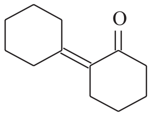
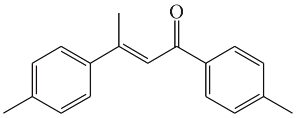
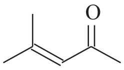
$$\text{BzOH} + \text{H}^{+**} \rightarrow [\text{BzOH}_2]^{+**} \qquad (5)$$

$$[\text{Bz-OH}_2]^{+**} + \text{Bz-OH} \rightarrow \text{Bz-O-Bz} + \text{H}_2\text{O}^{**} + \text{H}^{+**} \qquad (6)$$

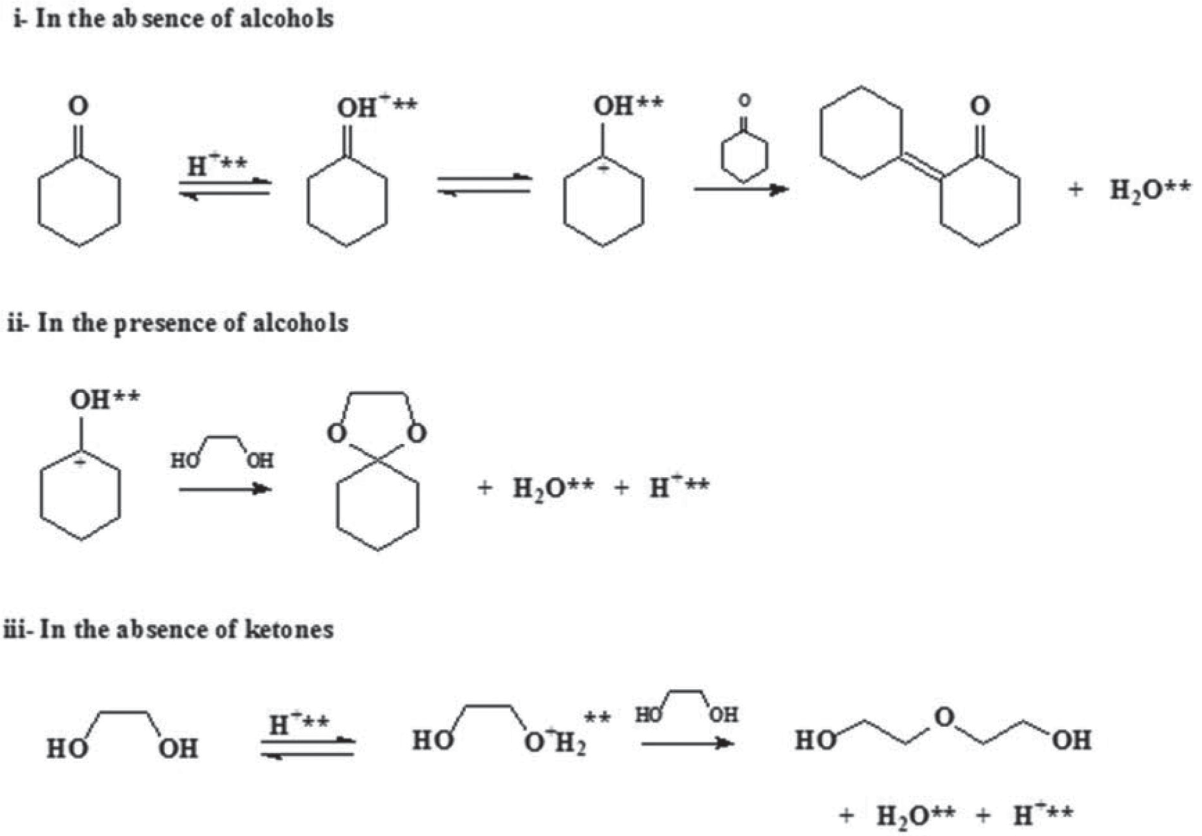
We propose that the catalyst is even more selective for the protonation of ketones over alcohols, and, therefore, the following sequence of reactions could apply, where ** stands for the catalyst bound species, Scheme 1.

An examination of the yields in Table 1 shows that, as the stability of the intermediates $[R_2C^+–OH]^{**}$ increases from $[Cy^+–OH]$ to $[Ph_2C^+–OH]$, the yields of the ketals decrease. This observation probably indicates that the catalyst holds those stable species more tightly. This effect, along with the difficult diffusion of glycerol through SiO_2-SO_3H in solvent-free reactions, also explains the lack of products in the reaction between benzophenone and glycerol. The six-membered ring ketals seemed to be preferred over the 5-membered ethylene glycol derivatives when the $[R_2C^+–OH]^{**}$ species are stabilized by aromatic rings, but this rule was not followed by glycerol, which gave exclusively the 5-membered ketal, entries 5-12 in Table 1. This is probably another evidence of the difficulty of the diffusion of the third CH_2–OH group of glycerol through the hydrophilic pores of the catalyst. It would seem, therefore, that the mesoporous sulfonated silica used as catalyst in this and previous works[7] showed a higher affinity for substrates following the order: organic acids < alcohols < ketones. The results suggest that the outcome of the reactions promoted by these highly hydrophilic catalysts are dependent on both the concentration of the catalyst and of the ratio of the reactants.

Table 2. Direct aldol condensation of acetone, cyclohexanone, acetophenone and *p*-methyl acetophenone with SiO_2-SO_3H catalyst using MW irradiation

(**18**)	(**19**)	(**20**)	(**21**)
			
95.3%	98.5%	96.1%	99%[a]
7 min	6 min	7 min	

[a] Conventional heating, 12 h, reflux.



Scheme 1.

Conclusions

For the first time it is reported that a mesoporous sulfonated silica with a small surface area, large pore diameters and high hydrophilicity presented a higher affinity for ketones than for alcohols and easily promoted aldol condensations when used in concentrations from 7 to 24% (m/m) to the concentrations of ketones. In the presence of the poly-alcohols ethylene glycol, glycerol, trimethylolpropane and neopentylglycol, the ketones acetophenone, *p*-methylacetophenone and benzophenone were converted to the respective ketals in reasonable to good yields. However, benzophenone failed to react with glycerol; pure alkyl ketones such as cyclohexanone were more easily condensed and ketalized. In the absence of ketones, ethylene glycol was smoothly converted to bisethylene glycol. All the reactions occurred within minutes under solvent-free conditions using microwave irradiation at 360 W.

Supplementary Information

Supplementary data (FTIR spectra and GC-MS) are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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