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Beta Zeolite as a Catalyst for the Preparation of Alkyl Glucoside Surfactants: The Role of Crystal Size and Hydrophobicity

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Zeolite H-beta is an active and selective catalyst for the acetalization of the glucose to form alkyl glucoside nonionic surfactants. The characteristics of size and polarity of reactants, intermediates, and products determine the strong influence of the textural properties of the catalyst (crystal size and adsorption properties) on activity, selectivity, and deactivation. For two series of zeolites with different concentrations of Si–O–Si connectivity defects an optimum in activity is found for intermediate Si/Al ratios, this optimum being reached at lower Si/Al ratios in the series with the lower defect concentration, i.e., in the more hydrophobic series. Thus, the optimum catalyst of the hydrophobic series is more active than that of the hydrophilic series, and it also shows a better resistance to deactivation.

INTRODUCTION

Surfactants are present in many products which are commonly and largely used in our society. For instance, they intervene in the composition of detergents, textile washing, cosmetic products, and even in food production. Their economical and ecological impact is especially important when used as detergents. In this case a very important property is the biodegradability which is related to the level of branching of the alkyl chain (1). This factor strongly determines the production process and becomes in many cases the controlling factor.

Recently alternative surfactants based on alkyl glucosides with an alkyl chain between C8 and C18 have been prepared (2). In this case glucosides derived from natural products can be used as building blocks for the preparation of nonionic surfactants which present excellent biodegradability and a low degree of skin and oral toxicity (3, 4).

We have presented in a recent work (5) that it is possible to prepare butyl glucosides by means of the Fisher reaction using zeolites as catalysts. These lower glucosides are fairly well soluble in a fatty alcohol and can be used as intermediates for the manufacturing of higher glucosides (6). While large pore acid zeolites were shown to be active catalysts, it was observed that the adsorption of reactants and products played an important role in the kinetics of the process and therefore determined the conversion and product selectivity. This is not surprising if one takes into account that the reaction occurs between a highly hydrophilic reactant (D-glucose) and a much less hydrophilic one (aliphatic alcohol), leading to a product which contains both hydrophilic and hydrophobic moieties. Meanwhile, in processes in which different-sized reactants and products intervene, it becomes of paramount importance to control the diffusion patterns within the pores of the zeolite, this being done by a combination of the adequate pore and crystallite size. Thus, it appeared to us that it should be possible to strongly affect the catalytic activity of zeolites for the preparation of aklyl glucosides by changing their textural and hydrophobic–hydrophilic properties. In this work we show that beta zeolite, conveniently modified along the lines presented above, appears as a very adequate catalyst to produce alkyl glucoside surfactants.

EXPERIMENTAL

Catalysts

In order to study the effect of the crystallite size, following the method presented in Ref. (7), we synthesized four beta zeolites with different crystal sizes (0.05–0.90 μm) and very similar Si/Al ratios (∼16). Scanning electron microscopy (ISI-SS60) was used to determine the crystal size and morphology. The physico-chemical characteristics of each one of these zeolites are given in Table 1.

In order to determine the role of the framework Si/Al ratio and of the hydrophilic–hydrophobic properties of the beta zeolite on the synthesis of glucosides, two series of samples with differnt Si/Al ratios were prepared. The first series (PS series) includes the zeolites obtained by dealumination of a starting beta zeolite (VALFOR CP 806 B-25) from PQ corporation, synthesized in the presence of sodium and tetraethylammonium (TEA) cations. The dealumination of the zeolite (8) was carried out by dispersing a 2-g sample in 250 ml of a solution of nitric acid; the concentrations used were 8, 9, 9.2, 9.25, 10, 11, and 11.5 *N* in order to obtain

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TABLE 1

Physicochemical Characteristics of H Beta Zeolite Catalysts

Zeolite	Particle size (μm)	Si/Al[a]
H beta-1	0.05	18
H beta-2	0.35	16
H beta-3	0.60	15
H beta-4	0.90	14

[a] Measured by elemental analysis.

materials with Si/Al ratios of 52, 88, 118, 123, 140, 200, and 260, respectively. The suspensions were heated at 353 K with stirring and maintained at this temperature for 4 h. After cooling to room temperature the resultant zeolites were recovered by filtration, washed with deionized water, oven-dried overnight at 343 K, calcined at 873 K for 3 h and stored at room temperature.

Beta zeolites prepared by the above method contain a large number of external and internal silanol groups, due to a large number of crystal defects generated during the synthesis, and the dealumination and calcination processes (see below). The presence of these silanol groups renders the samples hydrophilic and very high zeolite Si/Al ratios are needed in order to show some hydrophobicity. Owing to this limitation we tested a second series (S series) of beta zeolites free of connectivity defects in their as-made form, which were synthesized according to a method presented in Ref. (9). The chemical composition of the zeolites is given in Table 2.

^{29}Si MAS NMR spectra were recorded at 5 KHz spinning rate using a Varian VXR-YOOSWB spectrometer at 79.5 MHz, with 4.5 μs pulses of 2/5 Π rad and 60-s recycle delay.

Both, silanol groups and the acidity were monitored by infrared spectroscopy. The infrared spectra were recorded at room temperature in a Nicolet 710 FTIR using self-supported wafers of 10 mg $\cdot$ cm^{-2}. The calcined samples were outgased overnight at 673 K and 10^{-3} Pa dynamic vacuum; then, pyridine was admitted into the cell at room temperature. After saturation, the samples were outgased at 523 K for 1 h under vacuum, cooled to room temperature, and the spectra were recorded.

Thermogravimetric analyses (T.G.A.) were performed on the calcined hydrated samples using a Netzsch STA-409 EP instrument with a heating rate of 10 K $\cdot$ min^{-1}, an air flow of 100 ml $\cdot$ min^{-1}, and using 0.02 g of sample. Al was analysed by atomic absorption using a Varian Spectra A-10 plus.

Anhydrous α-D-glucose and *n*-butanol, obtained from Aldrich and Quimon, respectively, with a nominal purity $\geq$99%, were used without further purification. *p*-toluenesulfonic acid (p-TSA), used as a reference acid catalyst in the liquid phase, was obtained from Aldrich.

Reaction Procedure

The zeolite catalysts were activated *in situ*, in a 100-ml batch glass reactor, by heating 0.75 g of the beta zeolite at 353 K under vacuum (1 Torr) for 3 h. After this time, the system was cooled to room temperature; then *n*-butanol (50 ml, 0.54 mol) was introduced, followed by glucose addition (2.50 g, 0.014 mol). The reaction mixture was heated at 393 K for 4 h in a system equipped with a silicone oil bath, a magnetic stirrer, and a condenser. The catalyst was uniformly suspended as a slurry by stirring at 600 rpm. In a preliminary set of experiments (Table 3) it was found that when working at 600 rpm the reaction was not controlled by external diffusion.

The solubility of the glucose in the *n*-butanol increased once the products were formed, and when 15–20% of the conversion was achieved the glucose was already completely dissolved.

Samples were taken and analyzed at regular time intervals. The filtered zeolite remaining in the micro-syringe was extracted with methanol and water as the first and second solvents, respectively. The different products and those extracted with solvents were analyzed by HPLC, adding a known amount of methyl α-D-glucopyranoside as the internal standard.

At the end of the reaction, the mixture was cooled to room temperature, dissolved in methanol, and filtered. Then, the filtered zeolite was submitted to continuous solid–liquid extractions using micro-soxhlet equipment

TABLE 2

Chemical Composition of PS and S Series

PS series		S series	
Catalyst	Si/Al[a]	Catalyst	Si/Al[a]
Beta(PS)-5	52	Beta(S)-12	12
Beta(PS)-6	88	Beta(S)-13	29
Beta(PS)-7	118	Beta(S)-14	40
Beta(PS)-8	123	Beta(S)-15	52
Beta(PS)-9	140	Beta(S)-16	75
Beta(PS)-10	200	Beta(S)-17	92
Beta(PS)-11	260	Beta(S)-18	184

[a] Measured by elemental analysis.

TABLE 3

Influence of the Stirring Conditions on the Rate of the Glycosidation Reaction at 393 K and in the Presence of Beta(S)-14

Stirring rate (rpm)	$r_0 \times 10^4$ (mol min^{-1} g^{-1})
400	4.20
600	4.16
800	4.26

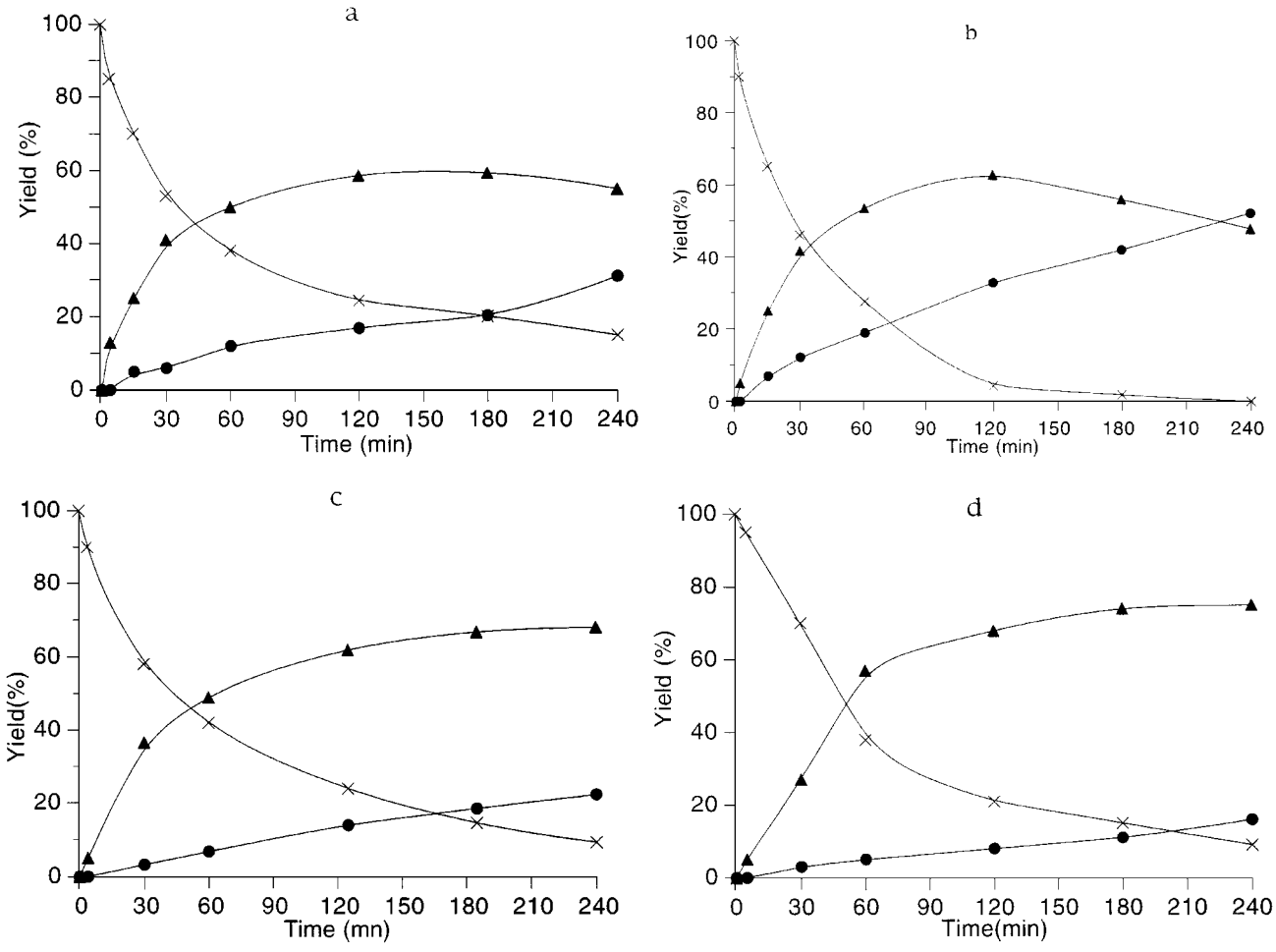


FIG. 1. Time conversion plot of D-glucose (×) to butyl glucofuranoside (**2**, ▲) and to butyl glucopyranoside (**3**, ●) at 393 K in the presence of H-beta zeolite of different crystal sizes: (a) 0.05 μm; (b) 0.35 μm; (c) 0.60 μm; (d) 0.9 μm.

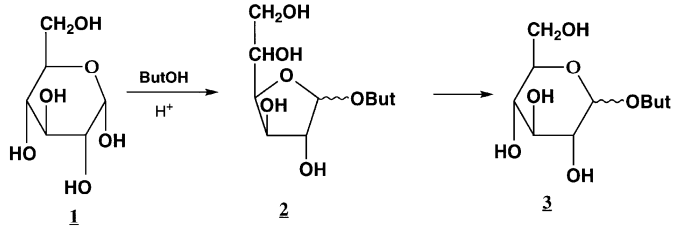
with methanol and water as the first and second solvents, respectively. The organic solutions were freed from the solvents and the remaining butanol by evaporation in a vacuum; they were combined, weighed, and analyzed by HPLC. Mass balances were performed in each experiment and the recovered products accounted for ≥95% of the reactants.

HPLC analyses were performed at 305 K on a system composed of a Waters pump (model 510) and a Waters 410 differential refractometer using a HYPERSIL-APS-25-mm (250 × 0.46 mm) column. In order to deal with the less polar products the column was eluted with an acetonitrile/water mobile phase composed of 7% water and 20% water for the more polar products, and in both cases the flow of the mobile phase was 1 ml/min. The preparative scale HPLC was performed using a HYPERSIL-APS-25-mm (250 × 1 mm) column and in this case the flow of the mobile phases was 4 ml/min.

The isolated products of the reaction were analyzed by means of ^{1}H and ^{13}C NMR spectroscopy, using a Varian 400 WB instrument, and were identified by comparing with data NMR spectra given in the literature (10).

RESULTS AND DISCUSSION

When the reaction between glucose and butanol was carried out on the H beta zeolite with a Si/Al ratio of 18 and a crystallite size of 0.05 μm, at 393 K, and using 1.5 wt% of catalyst, the result obtained (Fig. 1a) showed that two butyl glucoside isomers were formed (Scheme 1). The butyl



SCHEME 1

TABLE 4

Influence of Temperature and Percentage of H Beta Zeolite Catalyst on the Rate of the Glucosidation Reaction

Temperature (K)	Catalyst (%)[a]	$r_0 \times 10^2$ (mol min^{-1})	Yield[b]	
			2	**3**
383	1.5	1.15	34	65
393	1.5	5.06	20	78
393	3.0	10.31	6	90

[a] Percentage of catalyst related to the total weight of reactants.
[b] At 4-h reaction time.

glucofuranosides (α and β isomers) (**2**) appear as a primary and unstable product, while the behavior of the butyl glucopyranosides (α and β isomers) (**3**) better correspond to a secondary and stable product. This behavior agrees well with a reaction mechanism involving the fast formation of the five-membered rings compound, followed by the isomerization to the pyranoside product (11–15).

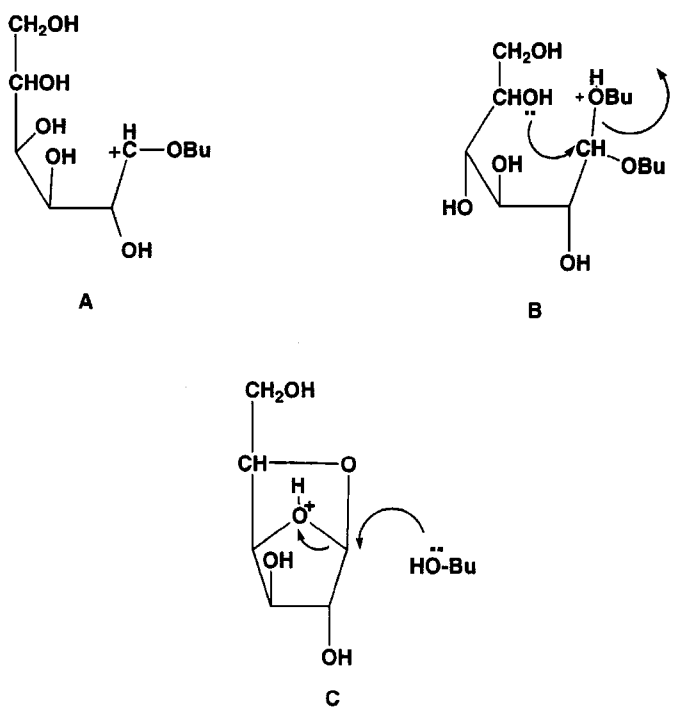
The presence of 5-hydroxymethyl furfural from the possible dehydration reaction of glucose was not detected in the reaction mixture.

The results given in Table 4 shows that a 10-degree increase in the reaction temperature produces a fourfold increase in the initial disappearance rate of glucose, which would give an apparent activation energy of $\sim$20 Kcal $\cdot$ mol^{-1}. This value is in good agreement with the activation energy obtained (22 Kcal mol^{-1}) when working in the liquid phase and using *p*-toluenesulfonic acid as the catalyst. The reaction appears to be first order with respect to the catalyst, as indicated by the fact that a twofold increase in the amount of catalyst produces a twofold increase in the initial reaction rate.

Influence of the Zeolite Crystal Size

In the case of reactions occurring in the liquid phase on a zeolite catalyst and involving reactants and/or products with molecular dimensions close to the diameter of the pores, the global reactivity shown by the catalyst can be strongly controlled by diffusional parameters. When special shape-selective effects are not required, but maximum reaction rate is desired, one has to decrease the influence of the diffusion through the micropores. This can be achieved by increasing the pore diameter of the zeolite and, for a given zeolite structure, by decreasing the length of the micropores, i.e., by decreasing the crystallite size. In the case of the acetalization of glucose we have varied the crystallite size of the beta zeolite in a wide range from 0.05 to 0.90 μm, while keeping constant the framework Si/Al ratio ($\sim$16). When the initial rates for the disappearance of glucose calculated from the slope of the curves at zero time were measured a similar reaction rate is observed for samples with 0.05 and 0.35 μm crystallite diameter (Figs. 1a, b). However, when the crystallite size was further increased, the initial reaction rate continuously decreased, indicating that the system is strongly influenced by diffusion for crystallite sizes larger than 0.35 μm (Figs. 1c, d). In other words, if maximum effectivity is wanted from a beta zeolite catalyst, samples with a crystallite size equal to or below 0.35 μm should be prepared.

When the influence of the crystallite size on the product distribution is considered (Figs. 1a–d) at conversions above 60%, the ratio of furanoside to pyranoside is practically the same for samples up to 0.35 μm and increases when increasing the crystallite size of the zeolite (Table 5). It appears then, when comparing the yields at the same level of conversion (Table 5), that the formation of pyranoside is more affected by diffusion than the furanoside. This can be caused by either a lower diffusivity of the somewhat larger six-membered ring pyranoside with respect to the five-membered ring furanoside, or by transition state restrictions for the ring expansion to occur inside the pores. The latter possibility would imply that most of the isomerization of the furanoside to the pyranoside form would occur on the external surface of the zeolite. At this point we have carried out a computer docking study (16) (Figs. 2a, c) which shows that while some geometrical restrictions for the ring expansion exist in the intersection of the 12-membered ring channel, at least when the most probable intermediates (12–15) were considered (Scheme 2), the diffusional problems along the 12-membered ring pores are larger for the pyranoside than for the furanoside alkyl



SCHEME 2

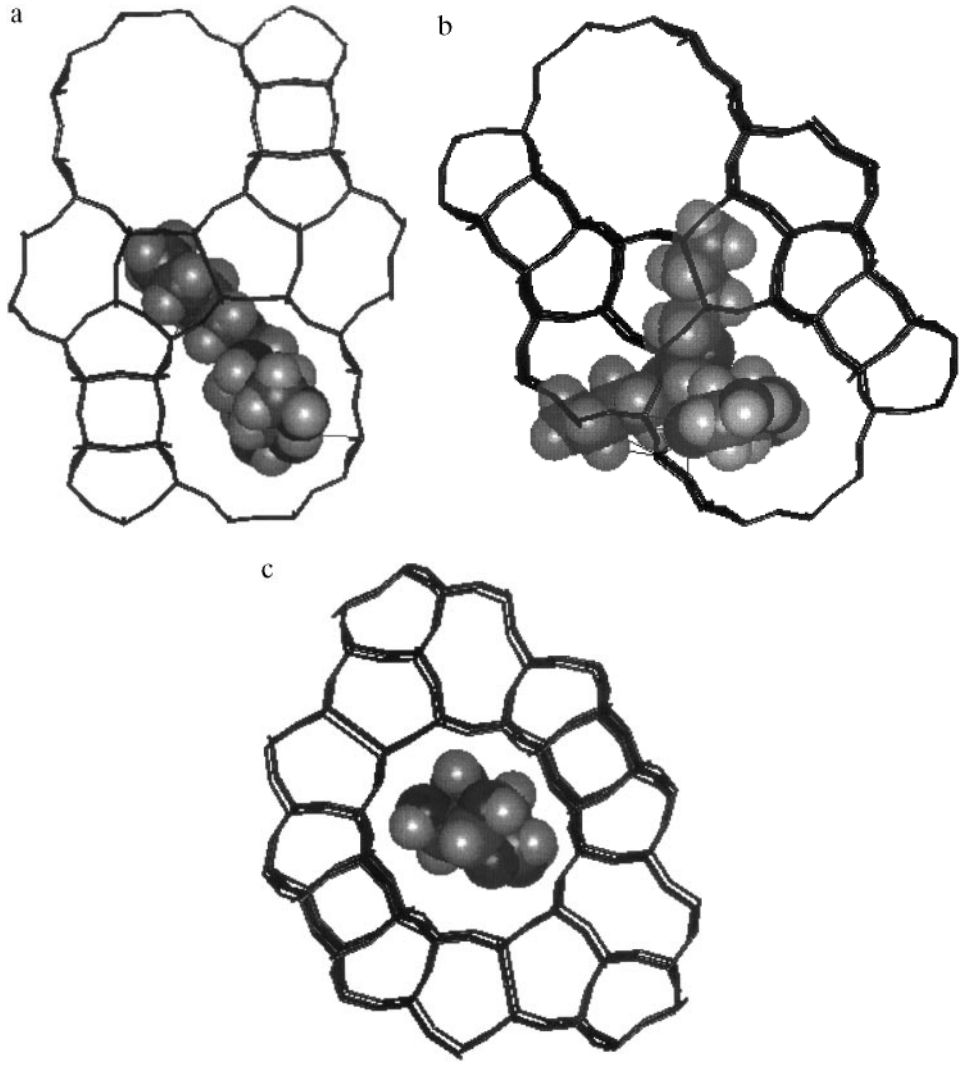


FIG. 2. Molecular modeling visualization of the most probable intermediates of reaction inside the cavity of the beta zeolite: (a) intermediate A; (b) intermediate B; (c) intermediate C.

glucoside (Figs. 3a, b). Thus, it is possible, by selecting the crystallite size of the beta zeolite, to control, not only its activity for the acetalization reaction, but also to change the product selectivity to the five or six membered ring alkyl glucosides. In any case, and as far as the surfactant properties are concerned, both furanoside and pyranoside compounds are of interest and, therefore, from a practical point of view one should use beta zeolite with crystallite sizes below 0.40 μm.

TABLE 5

Influence of the Zeolite Crystal Size on the Initial Reaction Rates (r_0, mol min^{-1} g^{-1}) and on the Products Distribution at 60% Glucose Conversion

Catalyst	Crystal size (μm)	$r_0 \times 10^4$ (mol min^{-1} g^{-1})	Yield (%)		
			2	**3**	**2/3**
H beta-1	0.05	4.9	50	10	5.0
H beta-2	0.35	5.2	48	12	4.0
H beta-3	0.60	3.7	55	5	11.0
H beta-4	0.90	1.8	57	3	19.0

Zeolite Framework Si/Al Ratio: The Influence of Hydrofobicity

A very important parameter which controls activity and selectivity when zeolites are used as acid catalysts is the framework Si/Al ratio. This parameter does not only define the number of potential protons, and therefore the number and strength of acid sites, but it also determines the adsorption properties of the zeolite (17, 18). The total number of acid sites will decrease when decreasing the number of framework aluminium or, what is equivalent, when increasing the framework Si/Al ratio. The strength of the acid

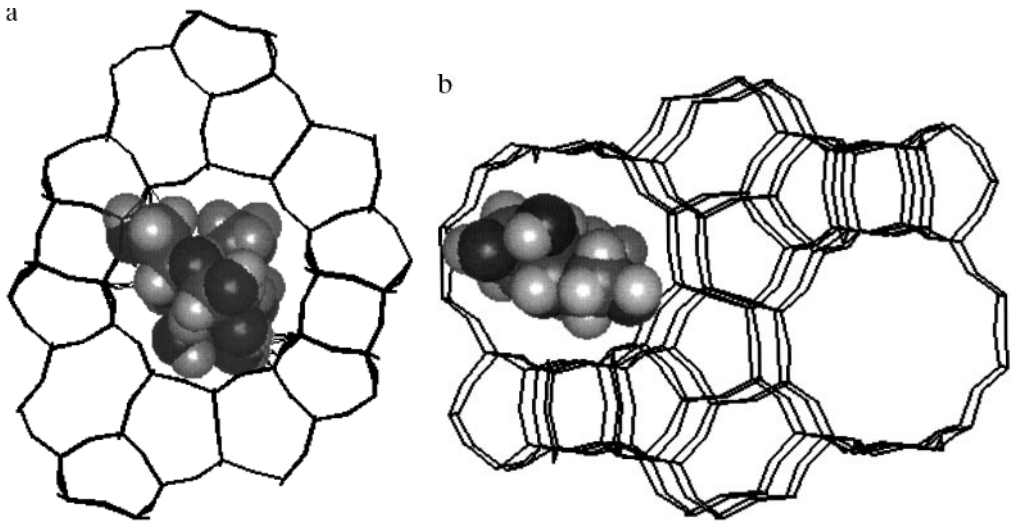


FIG. 3. Molecular modeling visualization of the: (a) butyl glucopyranoside and (b) butyl glucofuranoside inside the cavity of the beta zeolite.

sites will also depend on the aluminum content of the zeolite, the strength of the remaining acid sites increases when increasing the framework Si/Al ratio up to a certain value for which all Al will be isolated. At that point all the corresponding bridging hydroxyl groups should be equivalent with the maximum acid strength obtainable for a particular structure. In the case of the beta zeolite, it can be considered that practically all Al will be isolated for samples with framework Si/Al > 8. If this is so, one would expect the number of acid sites to continuously decrease in our samples when going from 52 to 260 Si/Al ratios for the PS series and from 12 to 184 Si/Al ratios for the S series, and consequently, the catalytic activity should decrease in the same way. The acidity of the catalysts was measured by IR spectroscopy, combined with the adsorption of pyridine and desorption at 523 K and the results show (Table 6) that the intensity of the pyridinium band and, therefore, the amount of pyridine bonded to Brönsted acid sites continuously decreases when decreasing the bulk Al content of the two zeolite series. The amount of pyridine bonded to Lewis sites was small due to the leaching of extra-framework Al (EFAL) by acid treatment in the PS series, and to the small amount of EFAL formed during the two-step activation of the samples in the S series. However, the catalytic activity does not follow the same behavior (Table 7). Indeed, concerning the PS series, the activity increases with dealumination until reaching a framework Si/Al ratio of 118. After this the activity strongly decreases.

TABLE 6

Brönsted Acidity (B.A.) of the Two Series Catalysts Measured by IR Spectroscopy Combined with Pyridine Adsorption and Desorption at 523 K

PS series			S series		
Catalyst	Si/Al[a]	B.A.[b]	Catalyst	Si/Al[a]	B.A.[b]
Beta(PS)-5	52	78.52	Beta(S)-12	12	229.52
Beta(PS)-6	88	66.44	Beta(S)-13	29	235.56
Beta(PS)-7	118	55.56	Beta(S)-14	40	144.96
Beta(PS)-8	123	53.15	Beta(S)-15	52	126.84
Beta(PS)-9	140	48.32	Beta(S)-16	75	84.56
Beta(PS)-10	200	30.2	Beta(S)-17	97	78.52
Beta(PS)-11	260	26.57	Beta(S)-18	184	30.2

[a] Measured by elemental analysis.

[b] Brönsted acidity (mmol Py/g catalyst) of the zeolite catalysts at 523 K; calculated using the extinction coefficients given in Ref. (19).

TABLE 7

Influence of the Framework Si/Al Ratio of the PS Zeolite Series on the Initial Rate and Yields in the Glucosidation Reaction between D-Glucose and *n*-Butanol at 393 K

Catalysts	Si/Al	$r_0 \times 10^4$ (mol min^{-1} g^{-1})	Yield (%)[a]	
			2	**3**
Beta(PS)-5	52	2.14	54	42
Beta(PS)-6	88	3.48	63	35
Beta(PS)-7	118	3.68	55	42
Beta(PS)-8	123	2.43	66	32
Beta(PS)-9	140	2.13	65	25
Beta(PS)-10	200	1.77	54	10
Beta(PS)-11	260	1.68	60	20
Beta(S)-12	12	3.17	48	50
Beta(S)-13	29	7.36	70	30
Beta(S)-14	40	4.16	52	48
Beta(S)-15	52	3.68	65	32
Beta(S)-16	75	3.50	63	30
Beta(S)-17	97	3.17	72	17
Beta(S)-18	184	1.84	65	13

[a] At 4-h reaction time.

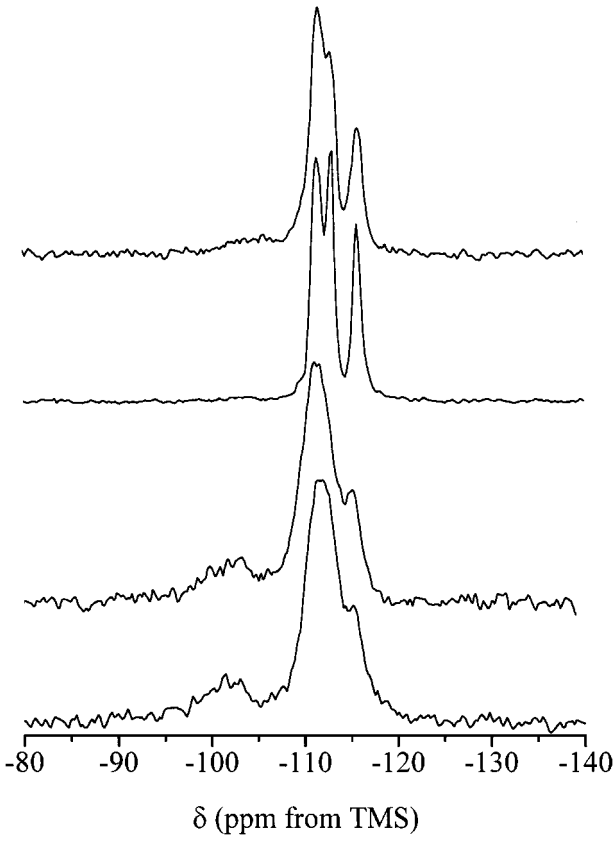


FIG. 4. ^{29}Si MAS NMR spectra of calcinated zeolite beta samples. From bottom to top: beta(PS)-9, beta(PS)-5, beta(S)-18, and beta(S)-15.

It is evident that the increase in activity when decreasing the framework Al content of the zeolite cannot be explained, taking only into account the variation in the number of zeolite active sites, but that some other factors play an extremely important role in this reaction. Indeed, we need to consider that for the reaction studied here a highly hydrophilic reactant (glucose) and a much more hydrophobic one (*n*-butanol) have to diffuse through the pores and adsorb in the zeolite. Thus in the case of hydrophilic zeolite samples glucose will be much more preferentially adsorbed and the reaction will become limited by the diffusion and the adsorption of *n*-butanol. If this is so it can be expected that an optimum in the adsorption characteristics of the zeolite should exist and this could be achieved by varying the hydrophobicity of the zeolite by dealumination. This effect is indeed observed by the reactivity and a maximum in activity is obtained for a framework Si/Al ratio of ∼118 rather than for a ∼12–16 value, as usually observed in most acid catalysed reactions on beta zeolites.

The beta zeolite PS series samples studied here contain a large number of crystal defects, as can be deduced from the relatively large intensity of the resonances at ∼−104 ppm, corresponding to Si (3Si, 1Al) + Si (3Si, 1OH) in the Si^{29} MAS NMR spectra (Fig. 4). These defects result in a large number of both free (band at ∼3740–3750 cm^{-1}) and hydrogen bonded (broad band centered at ∼3500–3600 cm^{-1}) silanol groups (Fig. 5) which introduce a hydrophilic character to the samples. This fact makes it necessary to strongly decrease the framework Al content in order to produce notable changes in the hydrophobicity of the samples and it explains the extremely high framework Si/Al ratio needed to produce a sample with adequate adsorption characteristics.

This hypothesis was confirmed by testing the second series of beta zeolites (series S). The ^{29}Si MAS NMR and IR results (Figs. 4 and 5) clearly show that these beta zeolites contain, after calcination, a very small concentration of silanol groups, as compared to the beta PS series. Thus, the ^{29}Si MAS NMR spectra (Fig. 4) show a much better resolution of Si (4Si) sites and a much smaller resonance at −102 to −105 ppm (corresponding to Si (3Si, 1OH) + Si (3Si, 1Al) for samples of the S series, as compared to PS series samples with the same bulk Al content (by chemical analysis). This is clearly due to a smaller concentration of SiOH defects in the series. Similarly, the IR spectra of the samples outgassed overnight at 673 K and dynamic vacuum (Fig. 5) clearly evidence that the S series samples contain

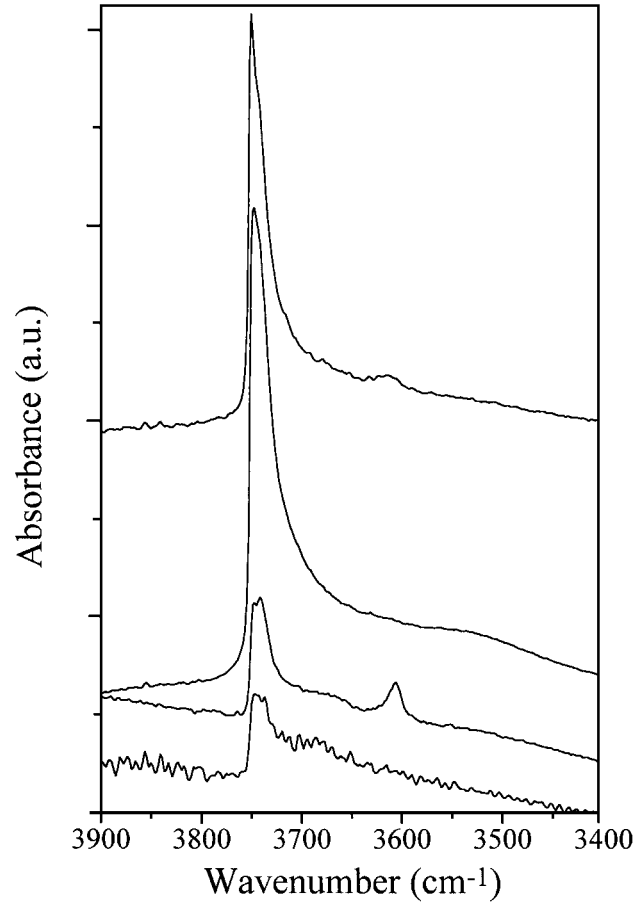


FIG. 5. IR spectra of the calcined zeolite beta samples outgassed overnight at 673 K and dynamic vacuum. From top to bottom: PS series with Si/Al = 52 and 140 and S series with Si/Al = 52 and 184.

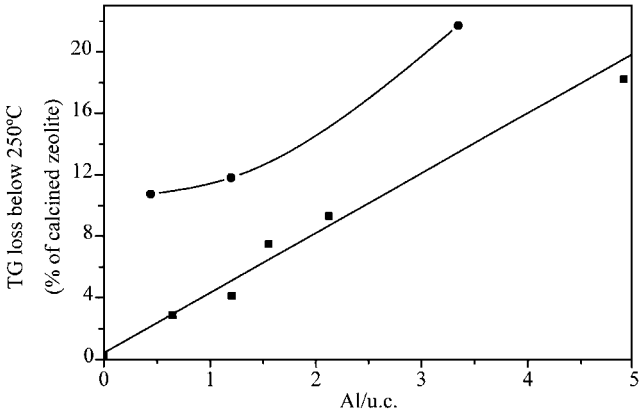


FIG. 6. Weight loss at temperatures below 523 K of calcined zeolite beta samples after rehydratation (●, PS series; ■, S series).

a smaller concentration of both free and hydrogen bonded Si–OH groups than the PS series samples with the same overall Al content.

This gives both PS and S beta zeolite series markedly different adsorpsion properties, the PS series being much more hydrophilic than the S series, as evidenced by the TG analysis of the fully rehydrated calcined samples (Fig. 6). The differences in hydrophobicity are reflected on their catalytic activity. Indeed, the results from Table 7 clearly show that in the most hydrophobic series (S), the maximum activity is achieved at a lower Si/Al ratio with the corresponding gain in activity with respect to the less hydrophobic PS series sample.

Catalyst Deactivation and Regeneration

Taking into account what has been said above, a too strong adsorption of reactants and products on the catalyst will decrease the reaction rate due to the reactively high value of the adsorption term in a Langmuir–Hinshelwood model:

$$r = \frac{kK_{AR}[R]}{1 + K_{AR}[R] + K_{AP}[P]},$$

where K is the kinetic rate constant, K_{AR} and K_{AP} are the adsorption constants for reactants and products, respectively, and $[R]$ and $[P]$ are the concentration of reactants and products.

Furthermore, this strong adsorption can also favour the production of polymerized products which will lead to the blockage of active sites and consequently to the poisoning of the catalyst. If such mechanisms would be responsible for the deactivation of zeolite beta catalysts during the formation of alkyl glucosides, it appears to us that one should expect a larger deactivation to occur on the PS series samples than on the S series samples. In order to check this hypothesis the two beta zeolites (PS-7 and S-13), corresponding to the maximum of activity of each series were subject after reaction to a repeated soxhlet treatment in order to extract possible products remaining adsorbed and which may cause deactivation of the catalyst. When this was done, the two catalysts were reused. The beta sample from the S series with a Si/Al ratio of 29, retained 45% of the original activity and still allowed us to reach, after 4 h reaction time, a total conversion of the glucose in butyl glucosides. On the other hand, the beta sample from the PS series with a Si/Al ratio of 118 was unable to fully catalyse the reaction, yielding only a 40% conversion after 4 h reaction time.

It is then clear to us that there is an optimum in the Si/Al ratio of the zeolite which matches two key properties, the number of active acid sites and the adsorption characteristics of beta zeolites, for the acetalization of glucosides to form alkyl glucoside surfactants. On top of that, the Si/Al ratio can also control the catalyst deactivation by decreasing the formation of high molecular weight products, either by decreasing their rate of formation and/or by increasing the rate of desorption.

CONCLUSION

In the present work we have shown that the preparation of alkyl glucoside nonionic surfactants can be catalyzed by BH zeolites. The study of the influence of the zeolite crystal size on the activity showed that the system is strongly influenced by diffusion for crystallite sizes larger than 0.35 μm. Moreover, the crystallite size has an influence on the product distribution and for crystallite sizes above 0.35 μm the ratio furanoside to pyranoside increases when increasing this parameter.

On the other hand, the study of the influence of the framework Si/Al ratio on the activity has shown that for the acetalization reaction of the glucose to form alkyl glucoside surfactants, there is an optimum in the Si/Al ratio of the beta zeolite which matches two key properties, the number of active acid sites and the adsorption characteristics. The fundamental importance of the adsorption properties of the catalyst is due to the different polarities of both reactants and we have shown that the optimum activity can be reached at lower Si/Al ratios when the catalyst contains a low concentration of Si–O–Si connectivity defects and, thus, a high hydrophobicity. Furthermore, the deactivation is strongly influenced also by the adsorption properties of the catalyst, its rate being lower the higher the hydrophobicity. Thus, the work presented highlights the crucial role that the control of the textural properties can play, in addition to the Si/Al ratio, in optimizing a zeolite catalyst for an industrially attractive reaction.

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