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Preparation of Environmentally Friendly Alkylglucoside Surfactants Using Zeolites as Catalysts

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Fischer glycosidation of D-glucose and *n*-butanol has been carried out successfully using different acid zeolites as catalysts. Both butylglucofuranoside and pyranoside are obtained during reaction. It has been found that large pore tridirectional zeolites with high Si/Al ratios such as faujasite and beta are the most suitable catalysts. The influence of the molar ratio alcohol/D-glucose on the selectivity to alkylmonosaccharide has been also studied.

INTRODUCTION

The long-chain alkyl D-glucosides are nonionic compounds with excellent surfactant properties, low toxicity, and good degradability. These carbohydrate derivatives have applications as cosmetic surfactants, food emulsifiers, and pharmaceutical dispersing agents (1, 2), for solubilization of phospholipid membranes (3), and their liquid crystalline properties have also been recognized (4).

Up to now, the most common procedure of preparation is Fischer–Helferich glycosidation which is a simpler and less costly method than the Koening–Knorr method. The Fischer–Helferich method involves the direct acid-catalyzed acetalization of a sugar, usually D-glucose, with an alcohol.

Several catalysts such as *p*-toluene sulfonic acid (*p*-TSA) (5, 6), sulfuric acid (5), hydrochloric acid (5), phosphoric acid (5), phosphorous acid (5), sulfonic acid (5–7), ion-exchange resins (5, 8), and amorphous silica–alumina (9) have been used with variable success. The main problem associated with these catalysts, with the exception of resins and amorphous silica–alumina, is the requirement of the final neutralization step. Moreover during the reaction, esters are produced from the alcohol and the acid catalyst, and they may cause the production of color bodies while making it difficult to determine the exact quantity of alkaline material needed to neutralize the acid. The use of resins avoids those problems by filtration, but it may promote the decomposition of the products at temperatures higher than 390 K, and they are not stable enough under reaction conditions upon long periods of use (9b).

The present paper describes the preparation of butylglucosides in the presence of zeolites as catalysts. The easy operation, stability, and shape-selective properties which can be used to avoid the formation of undesired products formed during the acetalization reaction make the zeolitic materials promising catalysts for producing alkyl D-glucosides.

EXPERIMENTAL

Materials

Five different zeolites topologies have been used in the present work.

The Na^+-exchanged HY zeolites (HY-50 and HY-100, where the number indicates the percentage of Na^+ exchanged) were prepared by stirring a commercial NaY sample (SK-40; Union Carbide, Si/Al = 2.5) with different aqueous solutions of ammonium acetate followed by calcination at 823 K (10, 11). A dealuminated HY-2 sample (Si/Al = 15.0) was obtained from PQ corporation (CBV-720).

The beta and ZSM-5 samples were supplied by PQ corporation, in the acidic form (H-beta) and in the ammonium form, respectively. The ZSM-5 sample was calcined at 823 K for 3 h to obtain the acid form (H-ZSM-5).

The acid form of mordenite (H-mordenite) was obtained, starting from a commercial Conteka sample in the ammonium form, by exchange calcination followed by acid treatment to extract the extraframework Al.

The MCM-22 sample was synthesized using hexamethyleneimine (HM) as template, following the procedure described in Corma *et al.* (12). The crystallization of the synthesis gel was performed in 60-ml Teflon-lined stainless-steel autoclaves at 423 K and 60 rpm for 7 days. After that, the solid was filtered, washed, dried at 353 K, and finally calcined in air at 853 K for 3 h to remove the organic material. The acid form of MCM-22 was obtained by two successive exchanges in a 2 *M* NH_4Cl solution at 353 K and a subsequent calcination step at 823 K for 3 h in air.

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TABLE 1

Physicochemical Characteristics of the Zeolite Catalysts

Zeolite	Crystallinity (%)	Particle size[a] (μm)	Si/Al[b]
MCM-22	90	0.35	15.0
HY-100	90	0.55	4.5
HY-2	90	0.55	15.0
H-ZSM-5	100	0.30	26.5
H-Beta	70	0.15	13.0
H-Mordenite	90	0.10	14.0

[a] Determined by SEM.

[b] Framework Si/Al ratios correspond to the values measured from the unit cell size dimensions and the Fichness–Schitler correlation (14) for Y zeolite and by chemical analysis for the rest.

A commercial sample of amorphous silica–alumina (25 wt% Al_2O_3) was supplied by Crosfield (surface area, 268 m^2g^{-1}).

The acidity of the final catalyst was measured by IR spectroscopy (Nicolet 710, FTIR spectrometer) combined with adsorption of pyridine and desorption at 623 K and 10^{-4} Torr. A more detailed description of the experiment procedure is given elsewere (13).

The physicochemical characteristics of all above zeolite catalysts are given in Table 1.

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

Reaction Procedure

The zeolite catalysts were actived *in situ* in a 10-ml batch glass reactor, by heating the zeolite catalyst at 353 K under vacuum (1 Torr) for 1.5 h. Then, the system was cooled to room temperature and *n*-butanol (5 ml; 54 mmol) was first added followed by the glucose (250 mg; 1.38 mmol). The mixture was heated at 383 K for 4 h in a system equipped with a silicone oil bath, magnetical stirrer, and condenser. The catalyst was uniformly suspended as a slurry in the butanol reaction solvent by stirring at 600 rpm. When the reaction started, part of the glucose was not dissolved. Its solubility increases when the products are formed. In this way, when the level of conversion was above 20%, the glucose was already completely solubilized. Samples were taken at regular times and filtered. The products were analyzed by HPLC. A known quantity of methyl-α-D-glucopyranoside was added as internal standard. At the end of the reaction, the mixture was filtered and cooled to room temperature. Then, the filtered zeolite was submitted to continuous solid–liquid extraction using micro-Soxhlet equipment and methanol and water as first and second solvent, respectively. The combined organic solutions were recuperated from the filtration and the Soxhlet extraction operations and were freed from the rest of the alcohols and dried by evaporation in vacuum to be analyzed by HPLC.

HPLC analysis were performed on a system consisting of a Waters pump (Model 510) and a Waters 410 differential refractometer. Two types of columns were used at 305 K to carry out these analyses. To purify the compounds of the reaction mixture, HPLC was performed using a HYPERSYL-APS 25-μm column (250 × 1.0 mm, Tracer). The same column, but with different size (250 × 0.46), was used for the analytic scale. In order to deal with the less polar products the column was eluted with an acetronitrile/water mobile phase composed of 7% of water and of 20% for the more polar products. In both cases the flow of the mobile phase was 1 ml/min.

The isolated fractions of the products of the reaction were analyzed by means of a ^1H and ^{13}C NMR Varian 400WB instrument and were identified by comparing with NMR spectra given in the literature (9).

RESULTS AND DISCUSSION

Reaction Scheme

In order to establish the reaction network for the acetalization of D-glucose (DG) by *n*-butanol (NB) on zeolites, kinetic experiments (Fig. 1) were carried out at an NB/DG ratio of 40 to avoid DG solubilization problems and the formation of oligosaccharides and butyl oligosaccharides. The reaction temperature was 383 K, and the catalyst was beta zeolite (1.5 wt%). The results given in Fig. 1 show that butylglucofuranoside, designated as **4**, appears as a primary product, while butylglucopyranoside, designated as **5**, is a secondary product. These results enabled us to present the reaction scheme (Scheme 1) for the acetalization of D-glucose by *n*-butanol on the zeolite catalyst. This reaction scheme has also been found to exist during the acetalization of different sugars such as D-glucose, D-xylose,

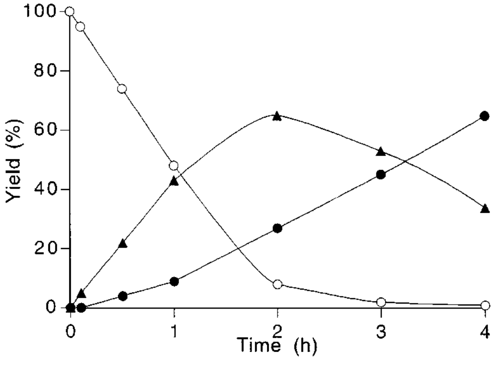
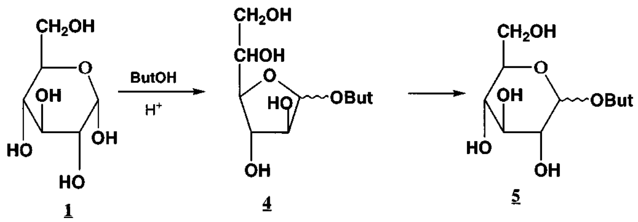


FIG. 1. Time conversion plot of D-glucose (**1**, ○) to butylglucofuranoside (**4**, ▲) and to butylglucopyranoside (**5**, ●) at 383 K in the presence of H-beta zeolite.



SCHEME 1

D-ribose, D-galactose, D-manose, D-lixose, and L-arabinose, with different alcohols and using liquid acids and resins as catalysts (14–16). This is an indication that the same type of acid sites and the same reaction mechanism should also operate in the case of zeolite catalysts. In this way (Scheme 2) during the first step, and in the presence of Brønsted acid sites, the intermediate aldehyde **2** reacts with the alcohol giving the two anomers hemiacetals **3**, which will rapidly evolve to give the butylglucofuranosides. These will go to a slow ring expansion reaction to give the corresponding glucopyranosides. The last step may occur by an endo as well as by an exocyclic rupture of the C–O bond (17–20). The above mechanism can explain both the formation of **4** as a primary product and the secondary character of **5**.

As stated above, strong acids, i.e., *p*-toluensulfonic acid, H_2SO_4, HCl, H_3PO_4, and sulfonic acids, have been used to catalyze this type of reaction. In the case of zeolites, the strength of the acid sites can be tuned in a certain range by changing the zeolite composition, and in this way it should be possible to select the most appropriate acidity to maximize activity and selectivity. In order to study this, the reaction was carried out using NaHY zeolites with two different degrees of ion exchange. It is known (21) that by decreasing the amount of Na^+ and increasing the amount of H^+ in exchangeable positions of zeolite Y, the total number of acid sites and also their strength increases. Then, regardless of acid strength, if all acid sites in NaHY zeolites are equally active for this reaction, a straight line correlation between the initial reaction rate for the formation of **4** and the amount of H^+ on the catalyst, i.e., percentage of Na^+ exchanged, should be observed. The results presented in Fig. 2 clearly show that the catalyst activity increases exponentially with the level of H^+ exchange indicating that not all acid sites are equally active for the acetalization of glucose, but mainly those with medium and high acid strength, should be the active ones.

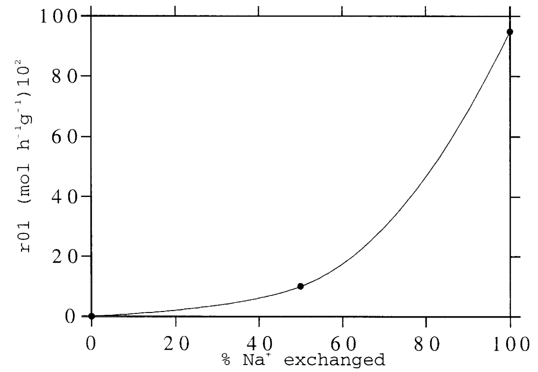
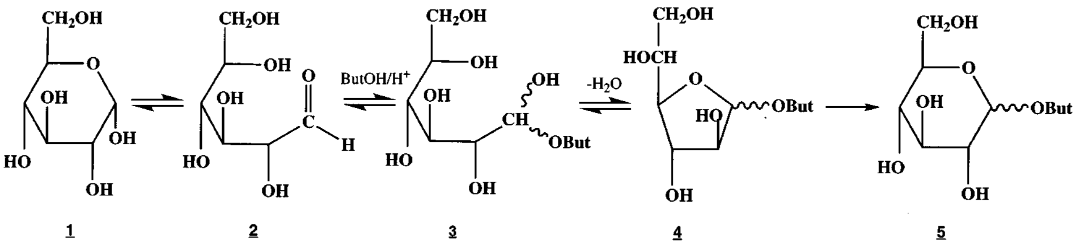


FIG. 2. Influence of Na^+ exchange level on the initial rate for butylfuranoside (**4**) at 383 K.

In the case of the reaction studied here, together with the acetalization of the D-glucose, there are other competing reactions which are undesirable leading to the formation of oligosaccharides and alkyloligosaccharides. It is apparent that in the case of the liquid acid catalysts, the extension of these undesired reactions will only depend on kinetic parameters, and little control could be exerted from the point of view of the catalyst. This should not be the case when using zeolites as catalysts, since the selection of an adequate pore structure could limit the formation of the bulkier transition state required to form the oligosaccharides. Following this idea we have selected a series of zeolites with different topologies: a 12-member ring (MR) unidirectional zeolite (mordenite), a 12-MR tridirectional zeolite with cavities (Y), a tridirectional 12-MR zeolite but without cavities (beta), one medium pore bidirectional zeolite (ZSM-5), and the recently discovered MCM-22 zeolite (22) which combines a 12- and a 10-MR system in its structure. The spectra of pore topologies and dimensions are broad enough to give a reasonable overview on the possibilities of zeolites as catalysts for the acetalization of D-glucose with alcohols.

The kinetic curves produced on each catalyst are given in Fig. 3, and initial rates for butylglucofuranoside calculated from the slope at Time zero of the curves and the rates at



SCHEME 2

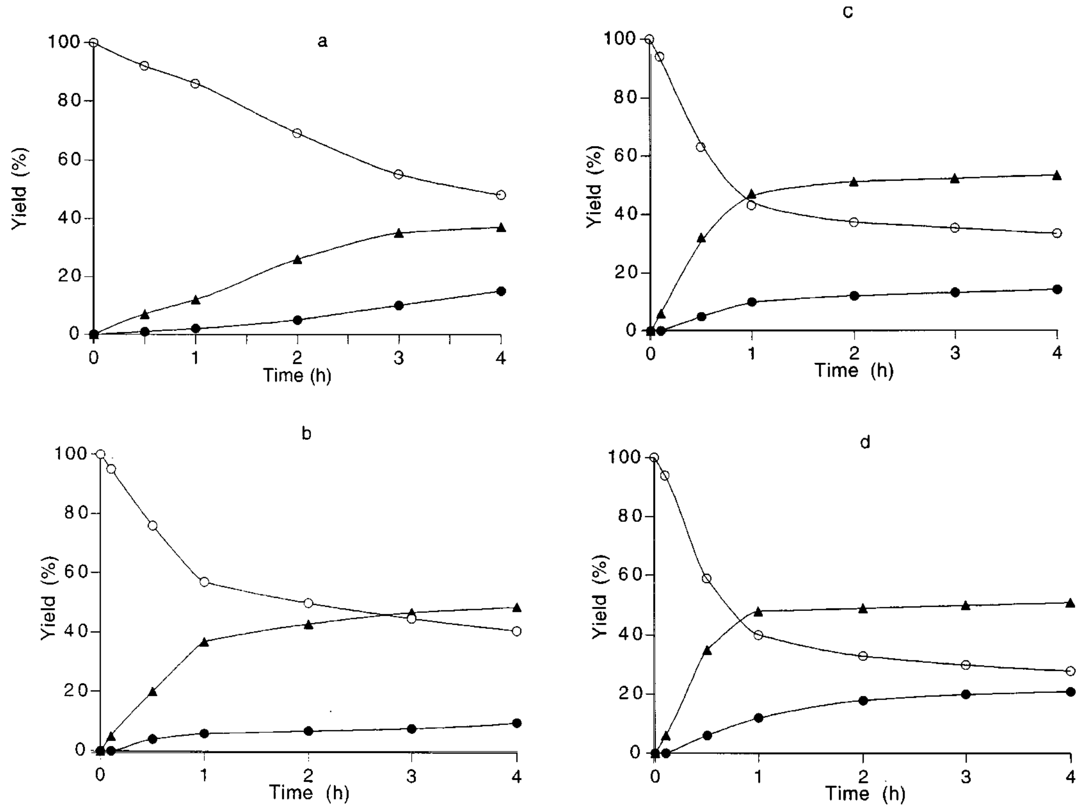


FIG. 3. Time conversion plot of D-glucose (**1**, ○) to butylglucofuranoside (**4**, ▲) and to butylglucopyranoside (**5**, ●) at 383 K in the presence of: (a) H-mordenite; (b) H-ZSM-5; (c) H-MCM-22; and (d) HY-100.

1 h reaction time for the butylglucopiranoside, as well as the yields to the different products obtained after a 4-h reaction time, are presented in Table 2. The order of activity is HY > MCM-22 > H-beta > H-ZSM-5 > H-mordenite. If one takes into account the number of Brønsted sites with medium and high acid strength of the different zeolites, measured by pyridine adsorption, and desorption at 623 K (Table 3), it can be seen that the order of catalytic activity cannot be explained by only taking into consideration the total number of potential active sites. Indeed, while the MCM-22 sample shows the largest number of potential active sites, it appears that the presence of the sinusoidal 10-member ring channels, as well as the 10-member ring windows which communicate the 12-member ring cavities, can decrease the rate of diffusion of products, decreasing therefore the efficiency of this zeolite. This effect is more clearly illustrated when the initial rate of butylglucofuranoside per Brønsted acid site is calculated (Table 3). The results show that now the order of activity is HY > H-beta > H-ZSM-5 > MCM-22 > H-mordenite. In other words, HY zeolite with large cavities communicated

TABLE 2

Initial Rates of Butylfuranoside (4), Rates at 1 h of Reaction Time for Butylpyranoside (5), and Yields of the Products Obtained in the Presence of Different Zeolites with NB/DG = 40 and at 383 K

	r_0 (mol h^{-1} g^{-1}) × 10^2		Yield (%)[a]	
Catalysts	**4**	**5**	**4**	**5**
MCM-22	84	13	52	14
HY-100	95	14	51	21
HY-2	60	17	23	65
H-ZSM-5	46	9	48	9
H-Beta	66	13	33	65
H-Mordenite	18	5	37	14

[a] Yield after 4 h of reaction.

TABLE 3

Initial Rate (r_{O1}) of Butylfuranoside (4) per Brønsted Acid Site in the Presence of Different Zeolites

Zeolite	Brønsted acidity[a] (Ba)	(r_{O1})/(Ba) (mol h^{-1}/μmol Py) × 10^2
MCM-22	41.28	2.03
HY-100	21.14	4.49
H-ZSM-5	21.14	2.31
H-Beta	27.18	2.43
H-Mordenite	21.14	0.85

[a] Acidity (μmol Py/g catalyst) of the zeolite catalysts at 623 K; calculated using the extinction coefficients given in Ref. (23).

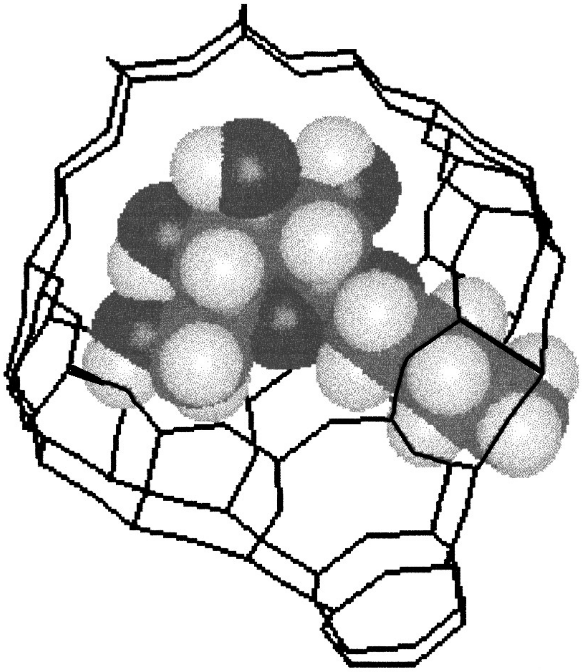


FIG. 4. Molecular modeling visualisation of the butylglucopyranoside (**5**) inside the cavity of the Y zeolite.

by large pore windows and, therefore, introducing lower diffusional restrictions than any of the other structures, gives the maximum initial activity per acid site (Fig. 4). After HY zeolite comes the H-beta zeolite, closely followed by H-ZSM-5 and MCM-22. The inadequacy of zeolites with an unidirectional pore system as catalysts for this reaction is shown by the low intrinsic activity of mordenite. This zeolite, while having the adequate acidity, appears as catalyticaly inadequate due to diffusional and counter diffusional limitations owing to the unidirectional system of channels.

On the other hand, the presence of 5-(hydroxymethyl) furfural from the possible dehydration reaction of glucose was not detected in the reaction mixtures. All the recovered products accounted for more than 95% of the mass.

For comparison purposes, the reaction was also carried out using *p*-toluensulfonic acid as homogeneous catalyst, and the initial rate for the disappearance of glucose was 30.36 mol h^{-1} per mole of H^+. This initial rate is much higher than the 4.74 mol h^{-1} per mole of H^+ calculated for zeolite HY-100. This fact is an indication that in addition to a possibly larger intrinsic activity of the *p*-TSA acid sites, limitations in the reactant accessibility to the acid sites in the case of the tridirectional HY zeolite should also play a role. If this factor will be the only one responsible for the observed lower reaction rate in the zeolite, we should conclude that only 15% of the theoretically available protons of the zeolite are acting in this reaction. Moreover, it should be taken into account that in the case of USY zeolites the number of available Brønsted acid sites is smaller than the number of framework Al, since part of those are replaced by AlO_2^+ type species formed during dealumination by steam.

Also on a comparative bases we have used an amorphous commercial silica–alumina with 25% Al_2O_3, and the results obtained give an initial reaction rate of 0.05 mol h^{-1} g^{-1}, which is much lower than that obtained with the zeolite catalysts.

Catalyst Stability

There is another reactivity feature which is worth discussing, and this is the evolution of conversion with reaction time. From Fig. 3d and Table 2 it is clear that while the initial activity of zeolite Y is the largest one, the reaction rate rapidly falls and becomes close to zero after 60% conversion. The loss of catalyst activity with time could be explained in this case by taking into account that the HY zeolite with relatively high density of acid sites is highly hydrophillic and, therefore, will form and strongly adsorb butylglucosides and oligosaccharides obtained as byproducts, decreasing the efficiency of the catalyst. This hypothesis is consistent with the fact that in the case of the beta zeolite, which has a higher nominal framework Si/Al ratio and therefore a more hydrophobic character, the final conversion achieved is higher than in the case of the HY-100 zeolite, even though the number of acid sites is much lower in the former zeolite catalyst.

In order to check the importance of the adsorption properties of the zeolites on their catalytic behavior, the HY-100 and H-beta zeolites used in the reaction were subjected to consecutive Soxhlet extractions with methanol and water. The total weight of the extracts was almost twice as high (1.5 g per g of zeolite) on HY than on beta zeolite. The influence of the framework Si/Al on catalyst activity preservation is clearly seen by comparing the behavior of the HY-100 with the HY-2 sample with a higher Si/Al ratio (Figs. 5 and 3d). The results show that while the initial activity of

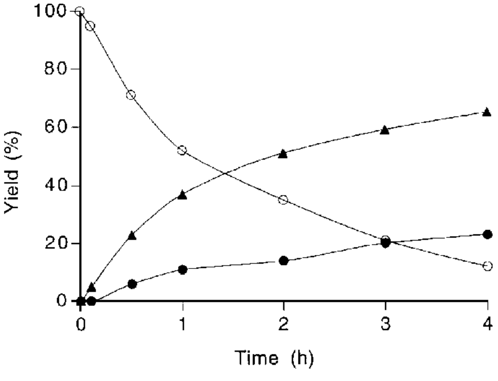


FIG. 5. Time conversion plot of D-glucose (**1**, ○) to butylglucofuranoside (**4**, ▲) and to butylglucopyranoside (**5**, ●) at 383 K in the presence of HY-2 zeolite.

the sample with a higher Si/Al ratio is lower, a smaller decrease of the rate of the reaction with time is obtained. On the other hand when the values of activities (initial rates for **4**) per framework Al are obtained, the activity per site is almost twice as large for the sample with a higher Si/Al ratio. This supports the hypothesis presented above in the sense that the acetalization reaction requires sites of medium and strong acidities.

In the case of H-ZSM-5, MCM-22, and H-mordenite, because of pore dimensions and topology it is clear that even relatively small amounts of strongly adsorbed products can severely limit the diffusion of reactants and products, affecting negatively the final conversion (Figs. 3a–3c). In conclusion, large pore tridirectional zeolites with high framework Si/Al ratios appear to be the most adequate catalyst candidates for carrying out the acetalization of D-glucose by *n*-butanol.

Influence of the Butanol/Glucose Ratio

From the point of view of the economy of the process it is important to minimize the alcohol to glucose ratio while keeping the rate of the reaction and the selectivity to alkylmonosaccharide at reasonable levels. In order to study that variable, the reaction was carried out using NB/DG ratios of 40, 20, 10, and 5 (mol mol^{-1}) on the H-beta zeolite catalyst at 393 K. The results from Fig. 6 clearly show that the initial rate for the formation of alkylglucoside increases up to a NB/DG ratio of 20 and then remains practically unchanged. The increase in the rate is much larger for the formation of the furanoside **4** than for the pyranoside **5**, something which can be easily explained from the accepted reaction mechanism (Scheme 2). Indeed, an increase in the concentration of alcohol will favour the ring opening, the formation of the hemiacetal anomers **3**, and the fast cyclation to the alkylfuranoside which will isomerize to give **5**.

With NB/DG ratios of 20 and 40, it is possible to obtain with 3% catalyst weight and 393 K conversions close to 100% with practically 100% selectivity to butylglycosides (Table 4). However, when NB/DG ratios of 10 and 5 were used and the amount of catalyst was increased to 6 and 12% in order to compensate the lower reactivity, it can be seen (Table 5) that the selectivity to butylglycosides decreases. Nevertheless, the selectivity obtained on the zeolite catalyst is sensibly higher than that obtained when using *p*-toluenesulfonic acid as catalyst (Table 5). Molecular docking simulations (24) (Fig. 7) indicate that the formation of oligosaccharides and alkyloligosaccharides is seriously restricted inside the pores of beta zeolite. Thus, it can be expected that the 4 and 7% of those products observed have been formed on the external surface of the zeolite. Therefore, it should be possible to optimize further the catalytic properties of the zeolites by poisoning the acid sites on the external surface and/or by dealuminating selectively the zeolite surface by postsynthesis treatments.

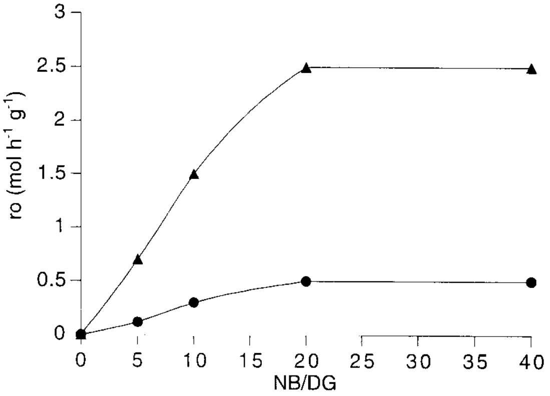


FIG. 6. Influence of the NB/DG relation on the initial rate (mol h^{-1} g^{-1}) of the butylglucofuranoside (**4**, ▲) and of the rate at 1 h reaction time for butylglucopyranoside (**5**, ●) at 393 K in the presence of H-beta zeolite.

TABLE 4

Initial Rates of Butylfuranoside (4), Rates at 1 h of Reaction Time of Butylpyranoside (5), and Yields at Different NB/DG Ratios in the Presence of 3 wt% of H-Beta Zeolite and at 393 K

	r_0 (mol · h^{-1} · g^{-1}) × 10^2		Yield (%)[a]	
NB/DG	**4**	**5**	**4**	**5**
40	140	40	3	95
20	226	65	4	93

[a] Reaction time, 4 h.

CONCLUSIONS

It has been shown that in the acid form zeolites are active and selective catalysts for the alkylglucosidation of the glucose by alcohols. During the reaction both alkyl glucofuranosides and pyranosides are formed.

Acid sites of medium strength are already able to carry out the reaction. However, hydrophilic zeolites are less ad-

TABLE 5

Comparison of the Yield and the Selectivity to Butylglucoside with Different NB/DG Ratios in the Presence of H-Beta and *p*-TSA at 393 K

			Yield (%)			
Catalyst	NB/DG	Catalyst (wt%)	**4**	**5**	Other[a]	Selectivity to (**4** + **5**)
H-Beta	10	6	12[b]	77	4	96
H-Beta	5	12	9[b]	78	7	92
p-TSA	5	1	7[c]	74	15	82

[a] The relative response of oligosaccharides and butylsaccharides to the internal standard was considerated as the same as the butylglucosides standard.

[b] Reaction time, 2 h.

[c] Reaction time, 1 h.

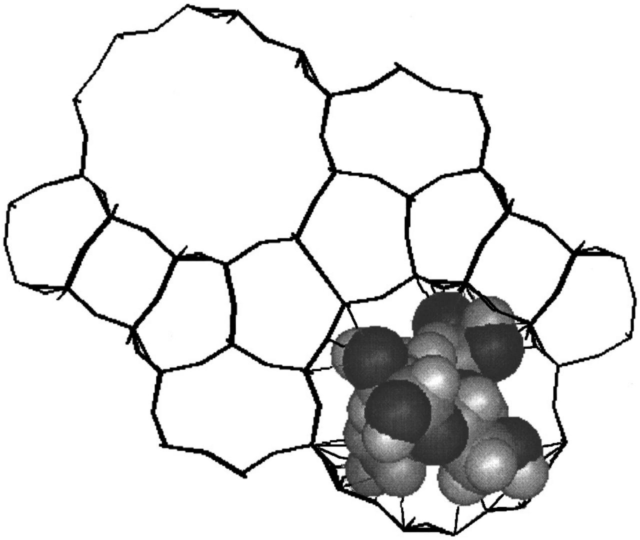


FIG. 7. Molecular modeling visualisation of a disaccharide inside the cavities of the beta zeolite.

equate due to the strong competitive adsorption of polar compounds. That is the reason why zeolites with high Si/Al ratios are preferred catalysts.

It is possible to avoid the formation of oligosaccharides and alkyloligosaccharides by using zeolites in where the bulkier transition states to those products is limited by shape-selective effects. From this point of view, and also considering the diffusion of reactants, it has been found that large pore tridirectional zeolites such as H-faujasite and H-beta are adequate structures.

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