Journal of Catalysis **183,** 76–82 (1999)
Article ID jcat.1998.2382, available online at http://www.idealibrary.com on IDEAL®

Mesoporous Materials as Catalysts for the Production of Chemicals: Synthesis of Alkyl Glucosides on MCM-41

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Received July 21, 1998; revised December 9, 1998; accepted December 9, 1998

The synthesis of alkylglucosides from glucose and *n*-butanol has been carried out successfully on Al–MCM-41 mesoporous materials. The influence of the chemical composition (Si/Al) and pore dimensions on activity and selectivity has been studied. It has been found that a higher concentration of acid sites does not guarantee a better catalytic performance, and the adsorption–desorption properties of the material play a determinant role in this reaction where the two reactants and the product have very different polarities. On the other hand, in the range of pore sizes studied here, the larger the diameter of the pore at the same level of Al contents, the more active is the final catalyst. The catalyst loses activity during the process due to the presence of strongly adsorbed molecules. Soxhlet extraction by methanol followed by water does not recover all the initial activity but produces a loss of crystallinity. However, the catalyst could be fully regenerated by calcination in air at 773 K. © 1999 Academic Press

INTRODUCTION

The synthesis of new mesoporous aluminosilicates molecular sieves of the M41-S family (1) with regular pore dimensions which can be varied between 2 and 10 nm has opened new possibilities in the field of solid acid catalysis (2). The system with a hexagonal array of pores known as MCM-41 is the most important member of the family and can be prepared by a liquid crystal templating mechanism where surfactant molecules act as templates (3). These materials, with mild acidities, were conceived initially to carry out catalytic cracking processes of bulky molecules. Unfortunately the hydrothermal stability of the material should be improved in order to prepare successful fcc catalysts (4). The advantages of mesoporous materials for acid catalized reactions, are based on the presence of large regular pores which allow the diffusion of reactants and conversely the fast diffusion of the products out, minimizing unwanted consecutive reactions and catalyst decay. If these characteristics are important in the field of oil refining and petrochemistry, they are still more important in the synthesis of chemicals and fine chemical products, which often involve bulky reactants and products. Furthermore, in many cases the synthesis of the chemicals is carried out in liquid phase where diffusional problems can be enhanced. While mesoporous materials have been extensively studied as catalysts for oil refining and petrochemistry, their use in the synthesis of chemicals and fine chemicals is still in its infancy (5–13).

Surfactants are present in many products which are commonly and largely used in our society. Long-chain alkyl glucosides are non-ionic compounds with excellent surfactant properties, biodegradability, and low degree of skin and oral toxicity (14, 15). They have several applications as cosmetic surfactants, food emulsifiers, and pharmaceutical dispersing agents (16, 17). Recently we have presented that is possible to prepare butyl glucosides in very good yields by means of the Fischer glycosidation reaction, using large pore acid zeolites as catalysts (18, 19). These lower alkyl glucosides, being more soluble than the glucose in a fatty alcohol, are important intermediates for the manufacturing of higher glucosides (20).

In this work we have investigated the possibilities of mesoporous MCM-41 aluminosilicates in the preparation of alkyl glucoside surfactants (21). Thus, we have carried out the acetalization of α-D-glucose with butanol in the presence of MCM-41, and we present the influence of the physicochemical characteristics of the catalyst on the activity and selectivity to butyl glucosides.

EXPERIMENTAL

Catalysts

The synthesis of Al containing MCM-41 catalysts with different pore diameters and varied aluminium contents was performed by controlling the chain length of the surfactant that templates the MCM-41 formation as well as the synthesis conditions.

Al–MCM-41 materials were prepared from the following general synthesis gel formulation: SiO_2, 0.28; TMAOH,

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0021-9517/99 $30.00

TABLE 1

Synthesis Conditions, Chemical Composition, Pore Diameter, and Surface Area of the Catalysts

Catalysts	n	x (10^2)	Crystallization T (K)	Crystallization Time (days)	Si/Al	Pore[a] diameter (nm)	S (m^2/g)[b]
MCM41-1	16	3.33	423	5	14	4.9	720
MCM41-2	16	2.0	423	5	26	5.4	624
MCM41-3	16	1.0	423	5	50	5.3	753
MCM41-4	16	1.0	408	1	51	4.5	835
MCM41-5	16	1.0	408	3	50	2.5	880

[a] Measured by Ar.
[b] Measured by N_2.

0.12; C_nTABr, 26.2; H_2O, $x Al_2O_3$, where x was varied in order to obtain Si/Al ratios between 15 and 50, and C_nTABr is an alkyltrimethylammonium bromide in which the linear alkyl chain contains 10 or 16 carbons atoms. The synthesis gel was prepared by adding a C_nTABr aqueous solution to an aqueous slurry containing 10 wt% of silica (Aerosil 200 from Degussa) and the appropriate weight of TMAOH (25 wt% solution in water, Aldrich). This slurry was further homogenized by stirring the mixture for 15 min. Then, the appropriate amount of aluminium source (Alumina Vista from Catapal) was added followed by the silica necessary to obtain the gel composition indicated in Table 1. The gel was homogenized for 1 h at room temperature by stirring at 250 rpm and autoclaved at 408 K during different crystallization times (see Table 1) in Teflon-lined stainless steel autoclaves. After crystallization, the Al–MCM-41 material was recovered by filtration, washed with distilled water, and dried at 333 K overnight. The final active acid Al–MCM-41 catalyst was obtained by removing the occluded surfactant, which fills the pores, by heating the sample under nitrogen at 810 K (temperature ramp $= 3°C\ min^{-1}$) for 1 h. Then, the remaining organic was burned off in air at 810 K for 6 h. The synthesis conditions for each particular MCM-41 catalyst, chemical composition, pore diameter, and surface area are reported in Table 1.

A beta zeolite with crystal size of 0.35 μm and Si/Al ratio of 16 was synthesized following the method presented in Ref. (22). Scanning electron microscopy (ISI-SS60) was used to determine crystal sizes and morphology.

The solids were characterized by X-ray diffraction on a Philips PW diffractometer using CuK radiation. Surface area measurements were obtained on an ASAP-2000 apparatus following the BET procedure. Pore diameter distribution was obtained using argon as adsorbate and following the Horvath–Kawazoe method (23).

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 for 16 h, and then pyridine was admitted into the cell at room temperature. After saturation, the samples were outgased at 423, 523, and 673 K under vacuum, cooled to room temperature, and then the spectra were recorded.

Anhydrous α-D-glucose and n-butanol, obtained from Aldrich and Quimon, respectively, with a nominal purity <99%, were used without further purification.

Reaction Procedures

Acetalization reaction of D*-glucose with n-butanol.* The catalyst was activated *in situ*, in a 100-ml batch glass reactor, by heating 1.5 g of the solid at 353 K under vacuum (1 Torr) for 3 h. After this time, the system was cooled to room temperature and then n-butanol (50 ml, 0.54 mol) was introduced followed by the addition of glucose (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.

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

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

At the end of the reaction, the mixture was cooled to room temperature, dissolved in methanol, and filtered. The filtered catalyst was submitted to continuous solid–liquid extractions in micro-soxhlet equipment using 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 vacuum. Then they were combined, weighed, and analyzed by HPLC. Mass balances were performed in each experiment and the recovered products accounted for more than 95% of the reactants.

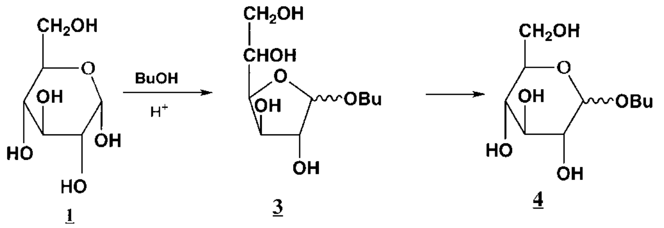
HPLC analysis were performed at 305 K on a system composed of a Waters pump (model 510) and a Waters 410 differential refractometer using a HYPERSIL-APS-25 mm (250 × 0.46 mm) column. In order to deal with the less polar products the column was eluted with an acetonitrile–water mobile phase composed of 7% of water, and 20% of water for the more polar products, the flow of the mobile phase being 1 ml/min in both cases. Preparative scale HPLC was performed using a HYPERSIL-APS-25 mm (250 × 1 mm) and in this case the flow of the mobile phase 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 they were identified by comparing with NMR spectra given in the literature (24).

Transacetalization of diphenylacetaldehyde (5) with TOF. Activation of the catalyst was performed *in situ* by heating the solid under vacuum (1 Torr) for 1 h. After this time, the system was left at room temperature and then a solution of the carbonyl compound (1.6 mmol) and trimethyl orthoformiate (TOF) (8 mmol) in tetrachloromethane (50 ml) as solvent was poured into the activated catalyst. The resulting suspension was magnetically stirred at reflux temperature for 5 h. Samples were taken at intervals and the reaction products were analyzed by gas chromatography (GC). At the end of the reaction the catalyst was filtered and washed with dichloromethane. The organic solution was concentrated in vacuum, and the residue was weighed and analyzed by ^{1}H-RMN and gas chromatograpy-mass spectrometry (GC-MS) using a Hewlett-Packard 5988 A spectrometer provided with a 25-m capillary column of cross-linked 5% phenylmethylsilicone. After reaction, the catalyst was submitted to continuous solid–liquid extraction with dichloromethane using micro-soxhlet equipment. After removal of the solvent the residue was also weighed and analyzed by GC-MS and ^{1}H-RMN. In all cases the recovered material accounted for more than 90% of the starting material. The ^{1}H-RMN analysis was carried out with a 400 MHz Varian VXR-400 spectrometer in deuterated trichloromethane and TMS as internal standard.

RESULTS AND DISCUSSION

The reaction between the α-D-glucose (1) and n-butanol (2) was carried out in the presence of a MCM-41 sample with a Si/Al ratio of 14 and a pore diameter of 4.9 nm, at 393 K. After 4 h of reaction the conversion of the glucose was practically quantitative and the only observed products were the anomeric mixtures of two butyl glucoside isomers, i.e., (α,β)-butyl glucofuranosides (3) and (α,β)-butyl glucopyranosides (4) (Scheme 1). In Fig. 1 the evolution of the reaction products versus time is represented. It can be seen there that (α,β)-butyl glucofuranoside (3) appears as a primary and unstable product while the behavior of 4 corresponds to a secondary and stable product. These results support a reaction mechanism involving the fast formation of the five-membered ring compound, followed by the ring expansion to the pyranoside product (25–29). The presence of 5-hydroxymethyl furfural coming from the possible dehydration reaction of glucose was not detected in the reaction mixture.



SCHEME 1

The catalytic active sites involved in the reaction should be acid sites associated to bridging hydroxyl groups, which in the case of the MCM-41 sample should be related to the presence of tetrahedrally coordinated Al in the amorphous walls forming the channels of the MCM-41 structure. The presence of the Brønsted-acid sites associated to Al^{IV} has been determined by pyridine adsorption (Fig. 2). The presence of a pyridinium band at 1545 cm^{-1} indicates the presence in the MCM41-1 sample of Brønsted-acid sites able to protonate pyridine which remains adsorbed after evacuation at 423 K. The presence of the 1455 cm^{-1} band corresponds to pyridine coordinated to Lewis sites, probably related with the presence of Al^{VI} generated during the calcination of the synthesized sample.

For comparative purposes, we have compared the results obtained on MCM41-1 with those obtained on a beta zeolite with a Si/Al ratio of 16 and crystal size of 0.35 μm. The results of the initial rates for the disappearance of glucose calculated from the slope of the curves at zero time and

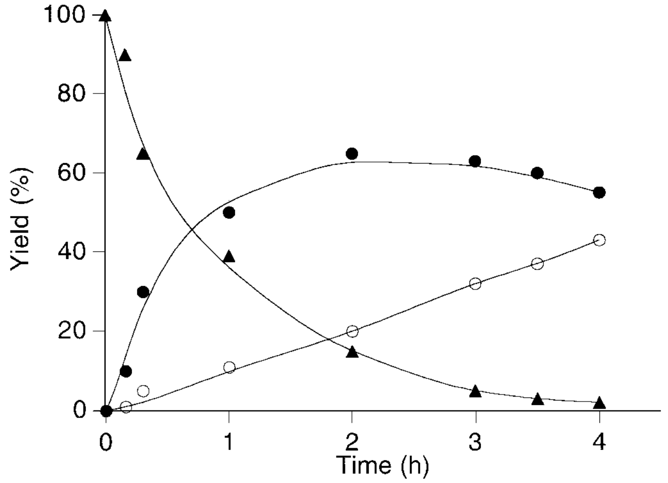


FIG. 1. Kinetic curves for the reaction of α-D-glucose and n-butanol on MCM-41-1 catalyst, at 393 K. (▲) α-D-glucose; (●) (α,β)-butyl glucofuranosides; (○) (α,β)-butyl glucopyranosides.

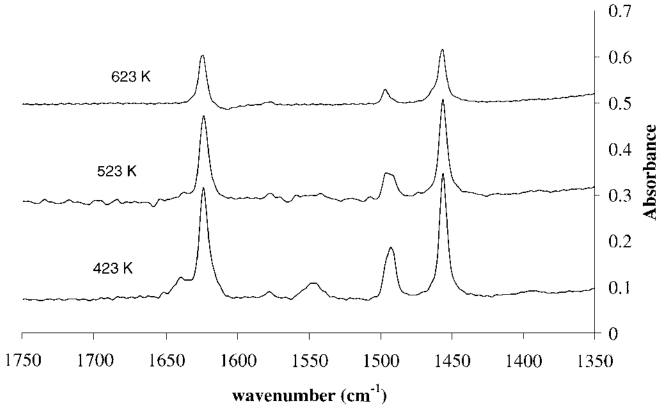


FIG. 2. IR spectra of pyridine adsorbed on MCM-41-1 at room temperature and desorbed at 423, 523, and 623 K.

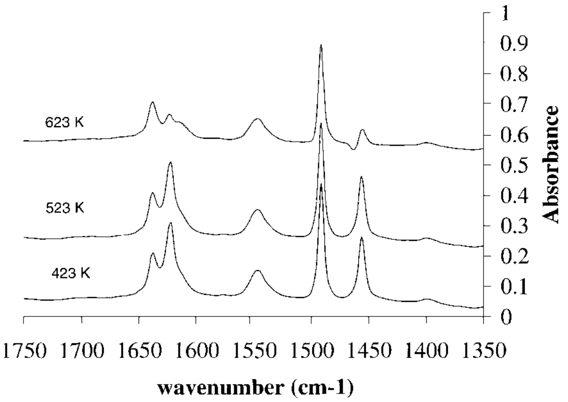


FIG. 3. IR spectra of pyridine adsorbed on a beta zeolite (Si/Al = 16) at room temperature and desorbed at 423, 523, and 623 K.

the yields of butyl glucosides are summarized in Table 2. It can be seen that beta zeolite is more active than MCM-41 and this result can be related with the presence of a much larger amount of bridging hydroxyl groups in the zeolites (Fig. 3). This observation is in agreement with the results obtained during the acetalization of aldehydes with different kinetic diameters (12), where it has been showed that when the reactants can diffuse inside the pores of zeolites, the microporous MCM-41 materials are more active than the mesoporous MCM-41 materials.

Influence of the Si/Al Ratio of MCM-41

In a recent work, we have presented that large pore zeolites were active catalysts for carrying out the acetalization of glucose with *n*-butanol, (19) and it was observed that the hydrophobic–hydrophilic properties of the solid play an important role in the kinetics of the process determining the conversion and product selectivity. It is known that the framework Si/Al ratio of molecular sieves is not only responsible for the acid but also for the hydrophobic–hydrophilic properties of the solids. Then, in order to study the influence of the Si/Al ratio on the catalytic activity of MCM-41, the reaction between D-glucose and *n*-butanol was carried out in the presence of three catalyst samples with Si/Al ratios of 14, 26, and 50 which have a similar pore diameter (~5.0 nm) (Table 1). In Table 3 the initial rates for the disappearance of glucose as well as the yields after a 4 h reaction time have been summarized. As we mentioned above, one would expect the number of acid sites to continuously decrease in the samples when going from 14 to 50 Si/Al ratios (Table 4), and for this reason the catalytic activity should decrease in the same way. However it can be seen in Table 3 that the activity of the catalysts increases when increasing the Si/Al ratio. It is evident that in order to explain the catalytic behavior, other factors besides the number of acid sites have to be taken into account. Thus, if one considers that the acetalization of glucose involves a highly hydrophilic reactant (D-glucose) and a much more hydrophobic *n*-butanol, we also need to consider the role played by the hydrophilic–hydrophobic properties of the catalyst on the relative adsorption of the two reactants. In this sense, it has been claimed (30, 31) that silica MCM-41 materials are hydrophobic in the sense that they adsorb a much larger amount of cyclohexane than water. However, when Al is introduced, the hydrophilicity of the material increases. This is even more so when some of the Al is removed from tetrahedral positions leaving a “nest”

TABLE 2

Initial Rates for the Disappearance of D-glucose and Yields of Butyl Glucosides Obtained in the Glucosidation of D-glucose with *n*-butanol in the Presence of Beta Zeolite and MCM-41-1 at 393 K, after 4 h Reaction Time

Catalyst	r_o 10^4 (mol min^{-1} g^{-1})	Yield (%)		Conversion (%)
		<u>3</u>	<u>4</u>	
Beta	5.2	48	52	100
MCM41-1	2.7	55	42	97

TABLE 3

Initial Rates for the Disappearance of D-glucose and Yields of Butyl Glucosides Obtained in the Glucosidation of D-glucose with *n*-butanol in the Presence of MCM-41 with Different Si/Al Ratios, at 393 K, after 4 h Reaction Time

Catalyst	r_o 10^4 (mol min^{-1} g^{-1})	Yield (%)		Conversion (%)
		<u>3</u>	<u>4</u>	
MCM41-1	2.7	55	42	97
MCM41-2	3.13	61	33	94
MCM41-3	3.68	39	59	98

TABLE 4

Brønsted Acidity (B.A.) and Lewis Acidity (L.A.) of the MCM-41 Samples Measured by IR Spectroscopy Combined with Pyridine Adsorption and Desorption at Different Temperatures

	423 K		523 K		623 K	
Catalyst	B.A.[a]	L.A.[a]	B.A.	L.A	B.A.	L.A.
MCM41-1	11.8	37.8	3.6	24.6	0	17.4
MCM41-2	8.3	11.0	2.8	12.3	0	7.4
MCM41-3	7.2	8.9	2.4	5.0	0	3.8
MCM41-4	7.1	10.6	3.5	8.5	0	5.1
MCM41-5	6.0	10.6	2.4	8.5	0	5.5

[a] Acidity (molPy/g catalyst) calculated using the extinction coefficients given in Ref. (32).

TABLE 5

Initial Rates for the Disappearance of Glucose and Yields of Butyl Glucosides Obtained in the Glucosidation of D-glucose with *n*-butanol at 393 K after 4 h Reaction Time, in the Presence of MCM-41 with Si/Al Ratio of 50 and Different Pore Diameters

		Yield (%)		
Catalyst	$r_0\,10^4$ (mol min^{-1} g^{-1})	**3**	**4**	Conversion (%)
MCM41-3	3.68	39	59	98
MCM41-4	2.30	58	36	94
MCM41-5	1.38	55	25	80

of silanol groups. If this is so, we could expect that in the higher Al content MCM-41 the more polar glucose could be preferentially and strongly adsorbed over the aliphatic alcohol, influencing negatively the diffusion–adsorption–desorption rates of reactants and products. This behavior can be changed by changing the framework Si/Al ratio of the catalyst. Then, when increasing the Si/Al ratio of the MCM-41 the hydrophobicity of the catalyst will increase, and the adsorption of the aliphatic alcohol as well as the desorption and diffusion of products will occur in a larger extension improving the catalytic behavior of the mesoporous material.

Indeed, it can be seen in Table 3 that the MCM-41 sample with the lowest content of Al, and therefore with the lowest content of Brønsted-acid sites, give nevertheless the highest conversion for the formation of glucosides. We correlate this increase in activity with the increase in the hydrophobicity of the sample, in agreement what we have observed when using a beta zeolite as catalyst (19).

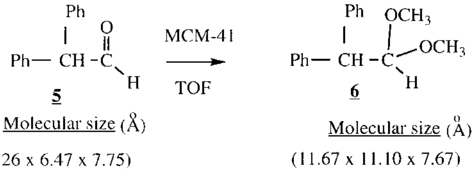
Influence of the Pore Diameter of the Catalyst

A characteristic of the mesoporous molecular sieves which is of paramount importance in organic synthesis is the possibility of modifying the dimensions of the pores in a wide range. Thus, depending on the molecular size of reactants and products, it is possible to select the most adequate pore diameter for a specific reaction.

In our case, and with the aim to study the influence of the mesopore diameter on the glucosidation reaction, the acetalization of D-glucose with *n*-butanol was carried out under the same experimental conditions, in the presence of three MCM-41 samples with the same Si/Al ratio (50) but with pore diameters of 2.5, 4.5, and 5.3 nm. If one would be working in gas phase and taking into account the relative size of the catalyst pores and the molecular diameter of reactants and products studied here, little, if any, influence of the pore diameter on the rate of the reaction could be expected. However in Table 5 one can see that a decrease in activity when decreasing the pore diameter occurs for the acetalization of glucose in liquid phase. Indeed, when the pore diameter decreases by a factor of two the initial rate becomes 2.5 times smaller.

In order to explain these results we have first of all looked into the concentration of acid sites present on the three samples. The pyridine adsorption results (Table 4) show that the acidity is very similar in all samples and in any case the small differences observed can not explain the large variation in activity. A further confirmation of this has been obtained by carrying out the transacetalization reaction of diphenylacetaldehyde (**5**) with trimethyl orthoformiate (TOF) (Scheme 2) on the three MCM-41 with different pore diameters. The aldehyde selected has no problems diffusing through the pores and at the same times does not present large differences in polarity when compared with the other reactant and with the reaction product **6**. The catalytic activity results presented in Table 6 shows that, as expected, the three MCM-41 samples with different pore diameters show very similar catalytic activity.

Thus, we have to conclude that the differences observed during the acetalization of D-glucose on MCM-41 samples with different pore diameter are not due to differences in the number of active sites, but have to be related with diffusional effects. Since owing to the size of the reactants and products obtained during the acetalization of glucose we should not expect differences in the diffusion coefficients on the three catalysts studied here, the following hypothesis has been made in order to explain the results obtained. In the case of the MCM-41, even for a sample with a Si/Al ratio of 50, some glucose is still strongly adsorbed in the pores of the catalyst. These strongly adsorbed molecules



SCHEME 2

TABLE 6

Initial Rates and Conversion after 4 h Reaction Time for the Transacetalization Reaction of Diphenylacetaldehyde (5) with TOF at 351 K in the Presence of MCM-41 with Si/Al Ratio of 50 and Different Pore Diameters

Catalyst	$r_0\,10^3$ (mol min^{-1})	Conversion (%)
MCM41-3	10.0	87
MCM41-4	9.3	85
MCM41-5	9.5	88

decreased the mean effective path way in the pores, introducing, therefore, diffusional limitations. These diffusional limitations will be smaller when increasing the pore diameter of the catalysts.

This hypothesis is not only reasonable, but it is also supported when considering the selectivity results obtained at the same level of conversion. In Table 7 one can see that the ratio of furanoside to pyranoside (**3**/**4**) increases when decreasing the pore diameter of the catalysts. It appears then that the formation of butyl glucopyranoside is more affected than the butyl glucofuranoside by the pore diameter, something which can be related to the lower diffusivity of the bulkier six-membered ring pyranoside with respect to the smaller five-membered ring furanoside (19).

Catalyst Deactivation and Regeneration

In order to study the catalyst deactivation occurring during the synthesis of alkyl glucosides we have carried out the acetalization of D-glucose with *n*-butanol in the presence of a MCM41-2 sample with a pore diameter of 5.4 nm and a Si/Al ratio of 26. After the reaction was completed, the catalyst sample was subjected to a soxhlet extraction with methanol and then with water. The resultant sample was again used in a second and in a third experiment. In Fig. 4 the conversion versus time obtained in each one of the three catalytic cycles is presented, and a decrease in activity when using the recovered catalyst is observed. Nevertheless, almost complete conversion is achieved in all cases after 4 h reaction time. This decrease in activity can be related with a loss of crystallinity and surface area of the catalyst, as a consequence of the successive soxhlet extractions with water. Indeed a strong decrease in the crystallinity of the sample has been observed after the soxhlet extraction treatments. It appears then, that a better catalyst regeneration procedure for this process could be burning of the products remaining adsorbed in the pores after completion of the reaction. When this was done by calcining the catalyst during 3 h at 773 K in air, the initial activity was restored.

TABLE 7

Influence of the Pore Diameter on the Products Distribution at 70% Glucose Conversion

Catalysts	Pore diameter (nm)	Yield (%)		
		3	**4**	**3**/**4**
MCM41-3	5.3	50	20	2.5
MCM41-4	4.5	55	15	3.6
MCM41-5	2.5	60	10	6.0

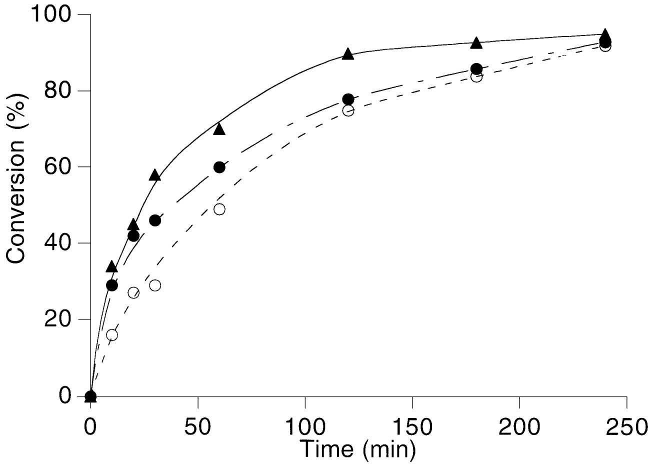


FIG. 4. Catalyst decay and regeneration by methanol and water soxhlet extraction. (▲) Fresh catalyst. (●) After a second use previous regeneration by soxhlet extraction. (○) After a third use previous a second regeneration by soxhlet extraction.

CONCLUSIONS

It has been shown that MCM-41 acid samples are able to carry out successfully the acetalization of glucose by aliphatic alcohols to produce biodegradable surfactants. For this reaction, the hydrophobic properties of the catalysts are as important as the concentration of active acid sites. In this sense samples with higher Si/Al ratios, at least in the range from 15 to 50, give higher conversions. Due to the strong adsorption of glucose, the mean free path through the channel could be diminished, and MCM-41 samples with larger pore diameters give higher conversions. Finally, the catalyst could be partially regenerated by carrying out a soxhlet extraction by methanol followed by water of the solid used in the reaction. However, this process produces the partial destruction of the MCM-41 and it is not the most adequate catalyst regeneration procedure. The catalyst can be conveniently regenerated by calcination in air at 773 K.

ACKNOWLEDGMENTS

Financial support by the Spanish MAT97-1016-C02-01 is gratefully acknowledged.

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