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Use of Delaminated Zeolites (ITQ-2) and Mesoporous Molecular Sieves in the Production of Fine Chemicals: Preparation of Dimethylacetals and Tetrahydropyranylation of Alcohols and Phenols

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Protection of aldehydes by formation of the corresponding dimethyl acetals and protection of alcohols and phenols by formation of the corresponding tetrahydropyranyl ethers have been carried out successfully using ITQ-2 zeolite as acid catalyst. Its catalytic activity for these reactions is compared with those obtained with MCM-22, Beta zeolites, and the mesoporous aluminosilicate MCM-41, all of them with similar Si/Al ratios. The results obtained indicate that when the reactions involve bulky reactants, ITQ-2 shows, in all cases, the highest activity as a consequence of the combination of its delaminated structure and the presence of strong acid sites.

INTRODUCTION

In recent years, environmental and economic considerations have created interest in the redesigning of commercially important processes in which the use of noxious substances and the generation of toxic wastes could be avoided. To this respect, there is no doubt that heterogeneous catalysts can play a key role (1) in the development of environmentally more friendly processes in petroleum refining and in the production of chemicals and fine chemicals. Among solid catalysts, zeolites have attracted special attention as acid, base, and redox catalysts. However, zeolites present some limitations when large reactant molecules are involved, especially in liquid-phase systems as is frequently the case in the synthesis of fine chemicals. Attempts to improve the diffusion of reactants to the catalytic sites have so far focused on increasing the zeolite pore sizes (2, 3), as well as decreasing zeolite crystal size (4). Recent work has described a new zeolitic material (ITQ-2) (5) in which a layered zeolite precursor is delaminated in much the same way as the layered structure of a clay may be unbound, resulting in an aluminosilicate whose zeolite-type catalytic sites are contained within thin, readily accessible sheets. Then the delamination process can improve the accessibility of the catalytic sites to large molecules (6).

Formation of acetals is one of the most useful protecting methods for carbonyl compounds (7), and a large amount of synthetic work has been done on the protection and masking of the carbonyl group. Acetals are important in carbohydrate (8) and steroid (9) chemistry. In the pharmaceutical (10), phytopharmaceutical, fragrance (11), and lacquer industries, acetals are used both as intermediates and as final products. The most general method for the synthesis of acetals is to react carbonyl compounds with an alcohol or an orthoester in the presence of acid catalysts, and in this sense *p*-toluensulfonic acid is often used (12).

Different solid catalysts such as silica gel (13), alumina (13), montmorillonite (14, 15) and Ce^{+3}-exchanged montmorillonite (16), sulfated zirconia (17), natural kaolinitic clay (18), Envirocat supported reagents (19), zeolites (20), and mesoporous aluminosilicates (21, 22) have been employed for the acetalization of carbonyl compounds using different reagents such as 1,2-ethanediol, methanol, ethanol, or trialkyl orthoformates, with variable success. As for the preparation of dimethylacetals, trimethyl orthoformate is widely employed as reagent on acid catalyst for the protection of aldehydes and ketones. Zeolites (20), hydrous zirconium oxides (23), clays (24), and mesoporous aluminosilicates (21) have been reported to be active catalysts for acetalization, achieving, in general, excellent conversions in relatively short reaction time and under mild conditions. Also, Ce^{+3}-exchanged montmorillonite (16) and mesoporous aluminosilicates (22) are able to catalyze with high performance (94–99%) the acetalization reaction of different aldehydes and ketones using methanol as dimethylacetalization reagent.

In another reaction, the conversion of alcohols to tetrahydropyranyl ethers is a generally used method of protecting hydroxyl groups, and tetrahydropyranyl ethers are important building blocks for the synthesis of primary alcohols (25), allyl alcohols (26), and alkyl halides (27). Due to the remarkable stability of tetrahydropyranyl ethers under a

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variety of conditions such as strong basic media, reduction with hydrides, oxidation and reactions involving Grignard reagents, lithium alkyls, and alkylating and acylating reagents, 3,4-dihydro-2H-pyran is the reagent of choice for hydroxyl group protection in peptide, nucleotide, carbohydrate, and steroid chemistry (28).

A variety of catalysts that are reported for the tetrahydropyranylation process include the use of Brønsted and Lewis acids (29, 30), aluminum phosphate (31), aluminum phosphate–aluminum trioxide (31), Envirocat EPZG (32), sulfonated charcoal (33), sulfuric acid adsorbed on silica gel (34), montmorillonite K-10 (35), sepiolite clay (36), zeolites (37), and the mesoporous molecular sieve (MCM-41) (38).

In the present work we have studied the catalytic possibilities of ITQ-2 for the protection of hydroxyl groups by formation of tetrahydropyranyl ethers, as well as for the preparation of dimethylacetals using trimethyl orthoformate (TMOF) as reactant. In this study we have prepared two ITQ-2 samples with different levels of delamination (ITQ-2-A and ITQ-2-B), and their activity for the preparation of dimethylacetals has been compared with those of the MCM-22 parent zeolite, a large pore zeolite (Beta), an amorphous silica–alumina, and a mesoporous molecular sieve aluminosilicate catalyst (MCM-41).

EXPERIMENTAL

Catalysts

An MCM-22 sample with an Si/Al ratio of 50 was synthesized following the procedure given in Ref. (39).

ITQ-2 samples were prepared by first synthesizing the MCM-22 laminar precursor (Si/Al = 50) and then swelling the precursor as described in Ref. (5). The laminar precursor was prepared in the following way: 0.23 g sodium aluminate (56% Al_2O_3, 37% Na_2O, Carlo Erba) and 0.8 g sodium hydroxide (98%, Prolabo) were dissolved in 103.45 g distilled water, after which 6.35 g hexamethyleneimine (HMI) and 7.86 g silica Aerosil 200 (Degussa) were added consecutively. The mixture was stirred vigorously for 30 min at room temperature, following by 11 days in a stirred PTFE-lined stainless steel autoclave at 408 K under autogenous pressure. The crystalline product was filtered and then washed with distilled water until pH < 9, and the filter cake was mixed with water to give a slurry with 20 wt% solids.

The swelling of the solids was carried out starting with a mixture of 27 g of slurry with 105 g of an aqueous solution of 29 wt% hexadecyltrimethylammonium bromide and 33 g of an aqueous solution of 40% tetrapropylammonium hydroxide for 16 h at 353 K. The completion of the swelling can be monitored by X-ray diffraction, which shows an increase in the distance between the layers from 2.7 to 4.5 nm. The layers are forced apart by placing the slurry in an ultrasound bath (50 W, 40 kHz) for 25 min and 1 h for ITQ-2-A and ITQ-2-B samples, respectively. A few drops of concentrated hydrochloric acid are then added until the pH is below 2, and the solids are collected by centrifuging. Organic material is then removed by calcination of the solids at 813 K, yielding ITQ-2 zeolite.

MCM-41 samples with Si/Al ratios of 40 and ∞ and with a pore diameter of 3.5 nm were prepared following the procedure given in Refs. (40) and (41), respectively.

Beta zeolite with an Si/Al ratio of 52 was prepared by dealumination of a starting Beta zeolite (VALFOR CP 806 B-5) from PQ Corporation by treatment with a solution of nitric acid as described in Ref. (42).

Amorphous silica–alumina with regular pores (1.5 nm) was prepared according to Ref. (43) and named SAM.

A commercial sample of amorphous silica–alumina (25% Al_2O_3) with a surface area of 214 $m^2 \cdot g^{-1}$ was supplied by Crosfield.

The solids were characterized by X-ray diffraction with a Philips PW 1710 diffractometer using Cu $K\alpha$ radiation. The IR spectra were recorded at room temperature in a Nicolet 710 FTIR using self-supported wafers of 10 mg cm^{-2}. The calcined samples were outgassed 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 outgassed at 423, 523, and 623 K under vacuum and cooled to room temperature; then the spectra were recorded. Absorption isotherms of N_2 were obtained on an ASAP 2000 apparatus after pretreating the samples under vacuum at 673 K overnight. The main characteristics of the samples used are summarized in Table 1.

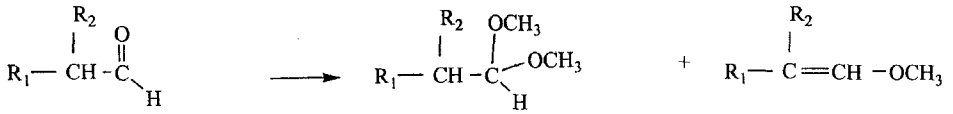
General Reaction Procedure

Acetalization of aldehydes with trimethyl orthoformate (TMOF) and tetrahydropyranylation of hydroxy compounds. Activation of the catalyst (30 mg) was performed *in situ* by heating the solid at 573 K under vacuum (6×10^2 Pa) for 2 h. After this time, the system was left at room temperature, and then the solution of the reactants was poured onto the activated catalyst. In the acetalization reaction, the amounts of reactants were carbonyl compound (2.5 mmol) and trimethyl orthoformate (TMOF) (12.7 mmol) in tetrachloromethane (25 ml) as solvent.

TABLE 1

Main Characteristics of the Samples

Catalysts	Si/Al	Surface area ($m^2\ g^{-1}$)	V_{Total} ($cm^3\ g^{-1}$)	External surface area ($m^2 g^{-1}$)
Beta	52	520	0.4550	95
MCM-22	50	457	0.5239	96
ITQ-2-A	50	585	0.6051	331
ITQ-2-B	50	768	0.8757	618
MCM-41	40	830	0.5800	830
SAM	50	719	0.4600	465
SiO_2/Al_2O_3	1.5	214	0.1618	183



	Molecular size (Å)	Molecular size (Å)	Molecular size (Å)
1	(12.05 x 3.97 x 5.29)	**1a** (13.29 x 6.79 x 4.31)	
2	(9.07 x 6.58 x 7.14)	**2a** (11.58 x 7.58 x 6.47)	**2b** (11.74 x 6.37 x 4.00)
3	(11.26 x 6.47 x 7.75)	**3a** (11.67 x 11.10 x 7.67)	**3b** (11.64 x 11.52 x 6.51)

	R_1	R_2
1	$CH_3(CH_2)_4$	H
2	Ph	CH_3
3	Ph	Ph

SCHEME 1

In the case of tetrahydropyranylation the amounts were hydroxy compound (3 mmol) and 3,4-dihydro-2H-pyran (DHP) (5.3 mmol) in hexane (25 ml) as solvent. The resulting suspension was magnetically stirred at reflux temperature. 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 NMR and gas chromatography–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 catalysts were submitted to continuous solid–liquid extraction with dichloromethane using a micro-soxhlet apparatus. After removal of the solvent the residue was also weighed and analyzed by GC–MS and ^{1}H NMR. In all cases the recovered material accounted for more than 90% of the starting material. The ^{1}H NMR analysis was carried out with a 400-MHz Varian VXR-400 spectrometer in deuterated trichloromethane and TMS as internal standard.

RESULTS AND DISCUSSION

Acetalization of Aldehydes with TMOF

Three aldehydes of different molecular size, heptanal (**1**), 2-phenylpropanal (**2**), and diphenylacetaldehyde (**3**) were reacted with TMOF on the different solid acid catalysts to produce the corresponding dimethylacetals. In the case of aldehydes **2** and **3** small amounts of the corresponding enol ethers **2b** and **3b** were detected in the reaction mixture (Scheme 1). The initial rate as well as the total conversion obtained after 1 h of reaction time are given in Table 2.

When the results obtained with the two zeolite catalysts with similar surface area and the same Si/Al ratio, MCM-22 and Beta, are compared, it is possible to see that in the case of the smallest reactant molecule, i.e., heptanal (**1**), the activity of Beta is larger than that of MCM-22 zeolite, despite the fact that the total numbers of Brønsted sites are similar (Table 3). These results indicate that diffusional constraints, especially for the reaction product, exist in MCM-22 even when the less bulky reactant is used (44). We have then

TABLE 2

Initial Rates and Conversion for the Acetalization of Aldehydes 1, 2, and 3 with TMOF over Different Acid Catalysts

	1		2		3	
Catalysts	ro (h^{-1})	Conversion[a]	ro (h^{-1})	Conversion[a]	ro (h^{-1})	Conversion[a]
Beta	450	90	108	40	48	27
MCM-22	150	40	55	23	50	25
ITQ-2-A	152	55	120	53	90	40
ITQ-2-B	420	95	330	85	210	75
MCM-41	210	80	180	70	180	71
SiO_2/Al_2O_3	56	22	55	22	20	10
ITQ-2(Si)	—	—	—	—	—	—
MCM-41(Si)	—	—	—	—	—	—
SiO_2	—	—	—	—	—	—

[a] One hour reaction time.

TABLE 3

Brønsted (B)[a] and Lewis (L)[a] Acidity of the Different Catalysts Measured by IR Spectroscopy Combined with Pyridine Adsorption–Desorption at Different Temperatures

	423 K		523 K		623 K	
Catalysts	L	B	L	B	L	B
Beta	23	27	14	23	18	12
MCM-22	15	25	11	21	9	15
ITQ-2-A	24	18	20	17	15	8
ITQ-2-B	21	19	12	11	14	6
MCM-41	11	7	9	3	6	0

[a] mmol Py/g catalyst. Calculated using the extinction coefficients given in Ref. (45).

to consider that in the case of MCM-22 an important part of the reaction occurs on the external surface of the crystallites.

It has been reported (5) that the structure of ITQ-2 likely consists of thin sheets (≅2.5 nm thick) with an hexagonal array of "cups" that penetrate into the sheet from both sides. These cups would have an aperture of ~0.7 nm, formed by a 12-membered ring ≅0.7 nm deep. The cups meet at the center of the layer, forming a double 6-ring window that connects the cups, bottom to bottom. As a result, a smooth, 10-membered ring channels system runs in between the cups, inside the sheet. Clearly, the benefit of this structure is the greater accessibility and the smaller diffusion path to active sites. Then, when a partial delamination of MCM-22 is carried out, the activity slightly increases (Table 2) even though the total number of Brønsted acid sites decreases by ~25% during the delamination (Table 3). It is then obvious that the number of accessible sites has increased due to the partial delamination of the structure as a consequence of the opening of the 12 MR cages and the formation of accessible 12-member ring cups, which are opened at the external surface. Indeed, the external surface of ITQ-2-A is larger than for MCM-22 (Table 1).

This effect is better seen when delamination is carried out further and sample ITQ-2-B is prepared. In this case, the external surface area is almost twice that of ITQ-2-A, and the initial rate obtained is also almost doubled.

It is interesting to note that MCM-41 sample, owing to its short-range amorphous characteristics, strongly dealuminates during the activation procedure, leading to a sample with lower and weaker acidity and consequently with a lower catalytic activity. A similar conclusion could be reached with the fully amorphous silica–alumina.

When the size of the reactants is increased we can observe a decrease in the activity of all zeolitic samples. The decrease is especially marked with Beta zeolite when the largest reactant molecule is reacted (**3**). This reactant can not penetrate into the 0.76 × 0.64 nm diameter of the 12 MR pores, and can only react in the pore mouth at the external surface. It is then not surprising that MCM-22, with an external surface area similar to that of Beta zeolite, gives in this case similar activity. The decrease observed with the ITQ-2 samples when the size of the reactants is increased is related to the presence of the 10 MR sinusoidal channels and of the 12 MR (0.7 × 0.7 nm) cups, which are now the main "pore mouth" at the external surface of these samples. It is clear that the reactants feel the dimensions of these cups that do not behave as pure external "flat" surfaces, as is the case with MCM-41, for which the relative decrease in activity is less notorious. Nevertheless, the fully delaminated ITQ-2-B sample shows, still, the highest activity for any of the studied reactants.

From a practical and environmental point of view, it is interesting to carry out the reaction in the absence of any solvent. Thus, we have performed additional experiments on the acetalization of diphenylacetaldehyde (**3**) with TMOF at 352 K without solvent and using ITQ-2-B as catalyst. The results from Fig. 1 show an initial reaction rate of 270 h^{-1} that is even higher than those obtained in the presence of the tetrachloromethane (see Table 2). It can be concluded that without solvent it is also possible to obtain high conversion and selectivity for acetalization reactions using ITQ-2-B as catalyst.

Tetrahydropyranylation of Alcohols

As we stated above, formation of tetrahydropyranyl ethers is a convenient method of masking hydroxyl groups. This protective group is introduced by an acid-catalyzed reaction between 3,4-dihydro-2H-pyran (DHP) and an alcohol (Scheme 2), while the deprotection step is usually carried out by an acid-catalyzed trans-tetrahydropyranylation with a simple alcohol such as methanol or ethanol.

In order to check the possibilities of ITQ-2 for catalyzing this reaction, the tetrahydropyranylation reaction of benzyl alcohol was carried out at 342 K using a small excess of DHP in the presence of ITQ-2-B as a catalyst and in hexane as solvent. In Fig. 2 the yields of the corresponding tetrahydropyranyl ether (**5**) versus time are plotted. It is

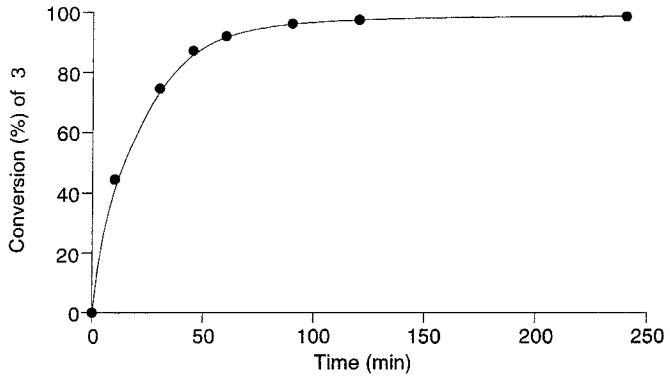
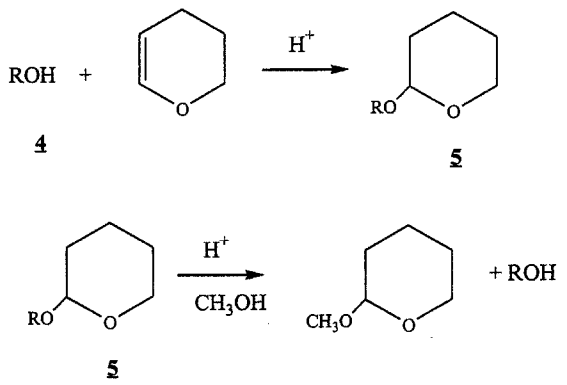


FIG. 1. Acetalization of diphenylacetaldehyde (**3**) with TMOF, in the absence of solvent at 352 K on ITQ-2-B zeolite.



SCHEME 2

possible to see that the catalyst shows an excellent activity and selectivity for this reaction, achieving a yield close to 100% within 30 min of reaction time.

For comparative purposes the reaction was carried out, under the same reaction conditions, using Beta, MCM-22, ITQ-2-A, and MCM-41 as catalysts, and the results are summarized in Table 4.

We can observe that the order of activity is ITQ-2-B > MCM-41 > ITQ-2-A > Beta > MCM-22. These results are in good agreement with those obtained in the acetalization reaction. Again, while the differences in the activity found for Beta, MCM-22, ITQ-2-A, and ITQ-2-B should be attributed to differences in reactant accessibility owing to the delamination of the structure, the higher activity of ITQ-2-B with respect to MCM-41 should be attributed to the existence of a larger amount of acid sites in the former sample, showing the higher stability of zeolitic versus short-range amorphous aluminosilicates toward dealumination.

A variety of alcohols with different molecular sizes and shapes were treated with 3,4-dihydro-2H-pyran in the presence of catalytic amounts of ITQ-2-B, and the corresponding THP-ethers (**5**) were obtained (Table 5). Both primary and secondary alcohols were converted into the corresponding THP ethers at reflux of hexane in good yields. In the case of menthol, the isopropyl group adjacent to

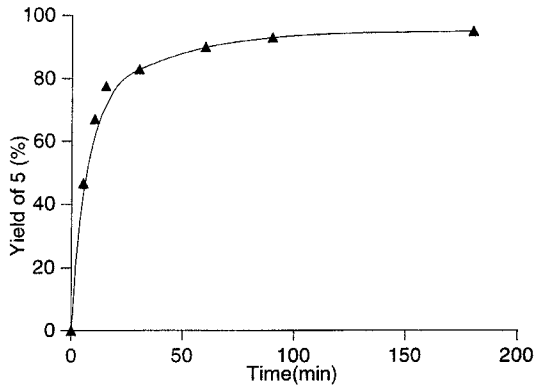


FIG. 2. Yield of tetrahydropyranyl ether **5** versus time obtained in the reaction of benzyl alcohol and DHP at 342 K in presence of ITQ-2 zeolite.

TABLE 4

Initial Rates (ro) and Yields Obtained in the Tetrahydropyranylation of Benzyl Alcohol by Different Catalysts

Catalysts	ro (h^{-1})	Yield (%)[a] of **5**
Beta	252	75
MCM-22	230	65
ITQ-2-A	362	85
ITQ-2-B	540	90
MCM-41	400	82

[a] Thirty minutes reaction time.

hydroxyl affected the reaction, thus inhibiting in some extensions the formation of THP ether, presumably due to steric hindrance. However, when the reaction was carried out without solvent the rate of the reaction and the yield of THP-ether were clearly improved.

For relatively less reactive alcohols, longer reaction times were necessary, and then the competitive bimolecular dimerization reaction of DHP began to be important. The extension of this parallel reaction could be decreased by keeping low the concentration of DHP by adding this reactant dropwise.

In general the reactions are reasonably fast, and even bulky molecules like 2-naphtol and cholesterol, which require several days to be completed when using conventional methods, are found here to give satisfactory yields in a few hours under mild conditions. These examples clearly illustrate the benefit of using delaminated zeolites, and more specifically ITQ-2, as acid catalysts.

For comparison purposes, the tetrahydropyranylation of cholesterol was carried out under the same reaction conditions, using as catalysts Beta zeolite, MCM-41, and an amorphous mesoporous silica–alumina (SAM) with an Si/Al ratio of 50 and a pore diameter of 1.5 nm. The results obtained are summarized in Table 6.

TABLE 5

Tetrahydropyranylation of Different Alcohols Using ITQ-2-B as Catalyst

Alcohol	Reaction time (min)	Temperature (K)	Conversion of **4**	Selectivity to **5**
Benzyl alcohol[a]	30	342	90	100
Ciclohexanol[a]	60	342	75	100
Phenol[a]	60	342	65	100
Menthol[a]	360	342	20	99
Menthol[b]	60	342	60	98
Cholesterol[c]	330	313	31	98
Cholesterol[c,d]	300	313	50	99
2-Naphtol[c,d]	240	313	51	90

[a] Reflux of hexane.
[b] Without solvent.
[c] Reflux of dichloromethane (10 ml).
[d] DHP was added dropwise within 90 min.

TABLE 6

Tetrahydropyranylation of Cholesterol with Different Catalysts

Catalysts	Reaction time (min)	Temperature (K)	Conversion of cholesterol	Selectivity to THP-ether
Beta	300	313	35	98
ITQ-2-B	300	313	50	99
MCM-41	300	313	55	98
SAM	300	313	12	98

TABLE 7

Study of the Reusability of Different Catalysts in the Acetalization of Aldehyde 3 with TMOF

	ro (h^{-1}) of **3**	
Catalysts	1st cycle	2nd cycle
MCM-22	50	40
ITQ-2(B)	210	205
MCM-41	180	160

It can be seen that while Beta zeolite and amorphous silica alumina (SAM) fail to efficiently catalyze this reaction, both ITQ-2 and MCM-41 give reasonable yields with good selectivity.

In conclusion, the use of ITQ-2 as acid catalyst provides a useful alternative to the preparation of tetrahydropyranyl ethers from bulky alcohols with the notable advantage that the work-up is reduced to a simple filtration with no need for acid removal or troublesome neutralization.

Study of the Deactivation and Reusability of the Catalyst

The deactivation and reusability of the catalysts were studied for the acetalization reaction of aldehydes with TMOF. Results from Fig. 3 show that in the case of the heptanal (**1**) deactivation of ITQ-2-B is very low, reaching practically quantitative conversion within 1 h reaction time. However, on the MCM-22 sample, a strong deactivation is observed, achieving a maximum conversion of 50%, which does not change with time. These results can be an indication that, even in the case of the smallest reactant, the products formed during the reaction can adsorb in zeolite MCM-22, blocking the pores and/or the active sites, leading to a loss of catalytic activity.

After each acetalization reaction of the aldehydes **1**, **2**, and **3** using ITQ-2-B as catalyst, the solids were subject to continuous solid–liquid extraction with dichloromethane using a micro-soxhlet apparatus. The extracted samples were used as catalysts in a second experiment, and the loss of activity (initial rate) found for the three aldehydes was very similar (≅10%). However, the initial activity was fully restored after calcination of the catalyst at 813 K.

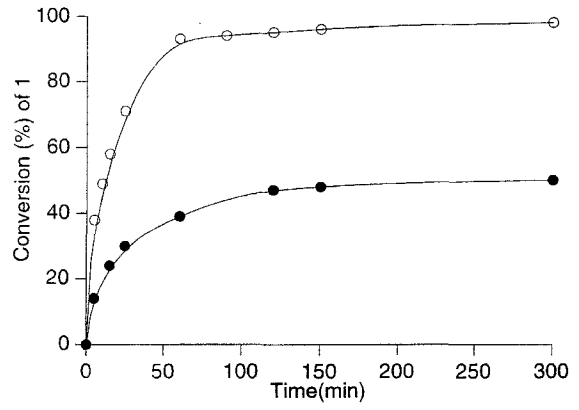


FIG. 3. Acetalization of *n*-heptanal (**1**) with TMOF on MCM-22 (●) and ITQ-2 (○).

For comparison purposes, MCM-22 and MCM-41 samples used for the acetalization reaction of the bulkiest aldehyde **3** were subject to continuous extraction as indicated above and were reused as catalysts in a second cycle. The results for initial activity obtained in the first and second cycle are summarized in Table 7. It can be seen there that both ITQ-2-B and MCM-41 show little deactivation as a consequence of the easy desorption–diffusion of the products. In a similar way, MCM-22 shows little deactivation when the bulkiest aldehyde **3** is used as reactant. This is not surprising if one considers that with reactant **3** the reaction can only occur at the cups located at the external surface of the crystallites, and therefore the adsorbed products should be easily removed.

CONCLUSIONS

It has been shown that the combination of zeolitic acidities, easy reactant accessibility, and fast desorption–diffusion of products are determinant issues for designing successful catalysts for acid-catalyzed reactions in the field of fine chemicals production. In this sense, delaminated zeolites, and more specifically ITQ-2, show excellent behavior for the preparation of dimethylacetals and for the tetrahydropyranylation of alcohols and phenols.

When the reactants and products can diffuse in and out of the structure, zeolites are very adequate catalysts for those reactions. However, when the size of the reactant increases, delaminated zeolites and mesoporous molecular sieves have clear advantages. In this case the zeolitic nature of the acid sites present in the delaminated ITQ-2 zeolite makes them more stable than those present in the short range amorphous MCM-41 molecular sieve, giving the former catalyst better activity and thermal regenerability.

ITQ-2 as well as MCM-41 are active and selective catalysts for acetalization reactions involving reactants as large as diphenylacetaldehyde and cholesterol.

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