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Food Chemistry 66 (1999) 301–306

Food Chemistry

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Isomerization of lactose catalyzed by alkaline-substituted sepiolites

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Received 9 September 1998; received in revised form and accepted 17 December 1998

Abstract

Strong base catalysts, prepared by substituting a part of the Mg^{2+} located at the borders of the channels of sepiolite with alkaline ions (Li^+, Na^+, K^+ and Cs^+), were investigated as catalysts for the isomerization of lactose to lactulose and epilactose. The activities exhibited by alkaline-exchanged sepiolites were significantly higher than that of natural sepiolite. The influence of temperature, time of the reaction and catalyst loading were also evaluated. A 20% conversion was obtained at 90°C at a catalyst loading of 15 g litre^{-1}. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Isomerization; Alkaline-sepiolite; Lactulose; Lactose; Epilactose

1. Introduction

As a consequence of cheese-making, high quantities of milk whey, containing about 5% lactose (4-*O*-β-D-galactopyranosyl-D-fructose), are produced. Lactulose, formed from lactose by isomerization in basic media, could find use in the food and pharmaceutical industries.

Natural silicates, especially clays, have good characteristics for use as catalysts for different organic reactions, including isomerization, hydration, dehydration and hydrogenation (Ruiz-Hitzky & Casal, 1985; Shukla, Verykios & Mutharasan, 1985). Sepiolite is a magnesium silicate currently used in a number of different applications, most of which are similar to those of the more traditional clays. New materials made of sepiolite are being investigated based on its cation-exchange capacity. Some of the Mg cations of sepiolite can be exchanged for catalytically significant species (Baldoví, Corma, García, Iborra, Miranda & Primo, 1992; Charlet & Manceau, 1994; Galán, 1996; Kazuo, Iida & Izumi, 1994; Kitayama, Muraoka, Kodama, Omi & Oizumi, 1996) such as Ni^{2+},CO^{2+}, Fe^{3+} and Cu^{2+}. The fixation of these ions confers higher catalytic activity on sepiolite. Replacement of Mg^{2+} by alkaline ions gives rise to strong base catalysts able to catalyse (at moderate temperature) the condensation of benzaldehyde with different ethyl esters (Corma & Martín-Aranda, 1991).

In a previous study (Troyano, de Rafael, Martinez-Castro & Olano, 1996), sepiolite was investigated as a catalyst for the isomerization of lactose and shown to possess activity in the temperature range 80–100°C. Since isomerization of aldoses is favoured in basic media, strong base catalysts such as alkaline-substituted sepiolites seem to be promising catalysts for carbohydrate isomerization. The present investigation studies the capability of alkaline-substituted (Li^+, Na^+, K^+ and Cs^+) sepiolites for lactose isomerization at moderate temperature.

2. Materials and methods

2.1. Materials

Sepiolite was supplied by Tolsa S.A. (Madrid, Spain) from its Spanish mines. It was a fine powder with the following physical properties: specific gravity, 2; apparent density, 100–120 g litre^{-1} and specific surface area (S_{BET}, N_2), 288 m^2 g^{-1} (González, Ibarra & Chamorro, 1987)

2.2. Alkaline-substituted sepiolites

The sodium form was prepared following the procedure previously reported (Mifsud, Corma & García, 1988): 100 g of natural sepiolite was heated at 120°C

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PII: S0308-8146(99)00060-6

with 1 litre 1 M NaOH for 1 h. After the ion-exchange, the resulting solid was thoroughly washed with distilled water.

The Li, K, and Cs forms of sepiolite were prepared by exchanging the Na^+ in the sodium form of sepiolite in a stirred 1 M solution of the desired alkaline cation, at 90°C, and a liquid to solid ratio of 10, for 1 h. After the ion exchange, the samples were washed and dried at 115°C for 15 h, according to Corma and Martín-Aranda (1991).

2.3. Treatments

Aqueous lactose solutions (5% w/v) were heated in a silicone bath at constant temperature. When the solution reached the desired temperature, an appropriate amount of the catalyst was added, the flask was sealed and the mixture stirred with magnetic stirrers. Samples of 2 ml were periodically withdrawn for analysis. Sepiolite loading varied between 0.9 and 30 g litre^{-1} of lactose solution.

2.4. Analytical determinations

The cation content of the alkaline forms of sepiolite was obtained by destroying the samples in hydrofluoric solution according to Barba and Valle-Fuentes (1986) and analysing the alkaline cation content by atomic emission spectrophotometry.

Disaccharides were analysed as their trimethylsilyl ethers on an OV-17 fused silica column at 240°C according to Olano, Calvo and Reglero (1986).

3. Results and discussion

Chemical analysis of the alkaline-substituted sepiolites showed differences in the meq/g of alkaline metals exchanged, the amount exchanged being higher in the Li-exchanged sepiolite than in the other alkaline ions assayed (Table 1).

Initial screening experiments for lactose isomerization were conducted at 100°C and a catalyst loading of 0.9 g litre^{-1}. The formation of lactulose and epilactose at different reaction times is shown in Figs. 1 and 2. These

Table 1
Alkali metal content of exchanged sepiolites

	Element (mmoles per 100 g)				
	Li	Na	K	Cs	Total
Sep-Li	114	12.4	28.9	–	156
Sep-Na	–	89.3	31.0	–	120
Sep-K	–	31.6	69.0	–	101
Sep-Cs	–	61.6	28.4	36.2	127

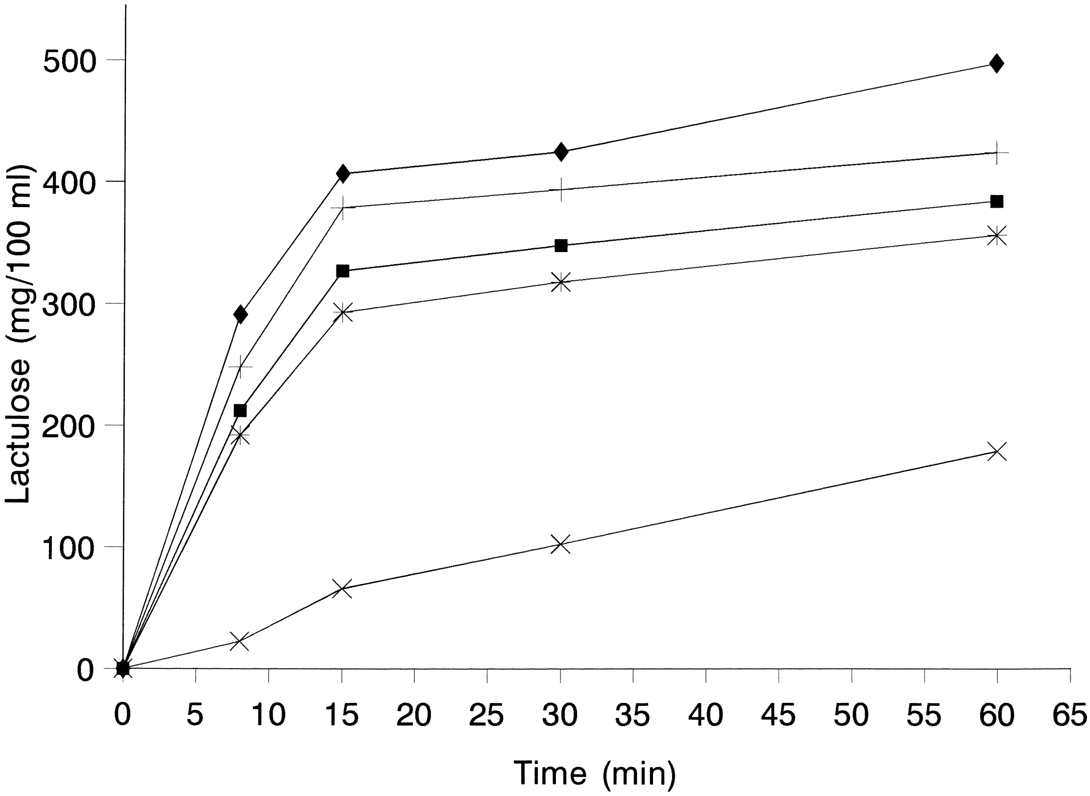

Fig. 1. Lactulose formed from 5% lactose solution at 100°C over 0.9 g litre^{-1} of natural sepiolite (-X-) and alkaline-substituted sepiolites with Li (-◆-), Na (-+-), K (-*-) and CS (-■-).

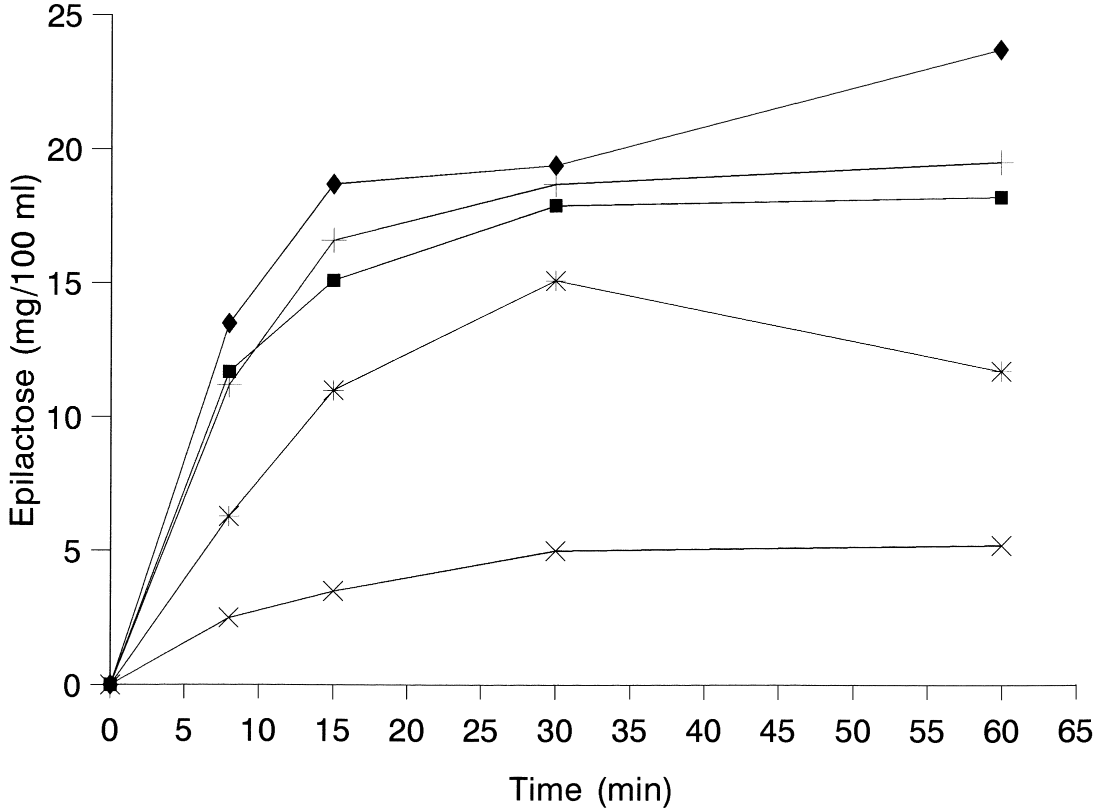

Fig. 2. Epilactose formed from 5% lactose solution at 100°C over 0.9 g litre^{-1} of natural sepiolite (-X-) and alkaline-substituted sepiolites with Li (-◆-), Na (-+-), K (-∗-) and CS(-■-).

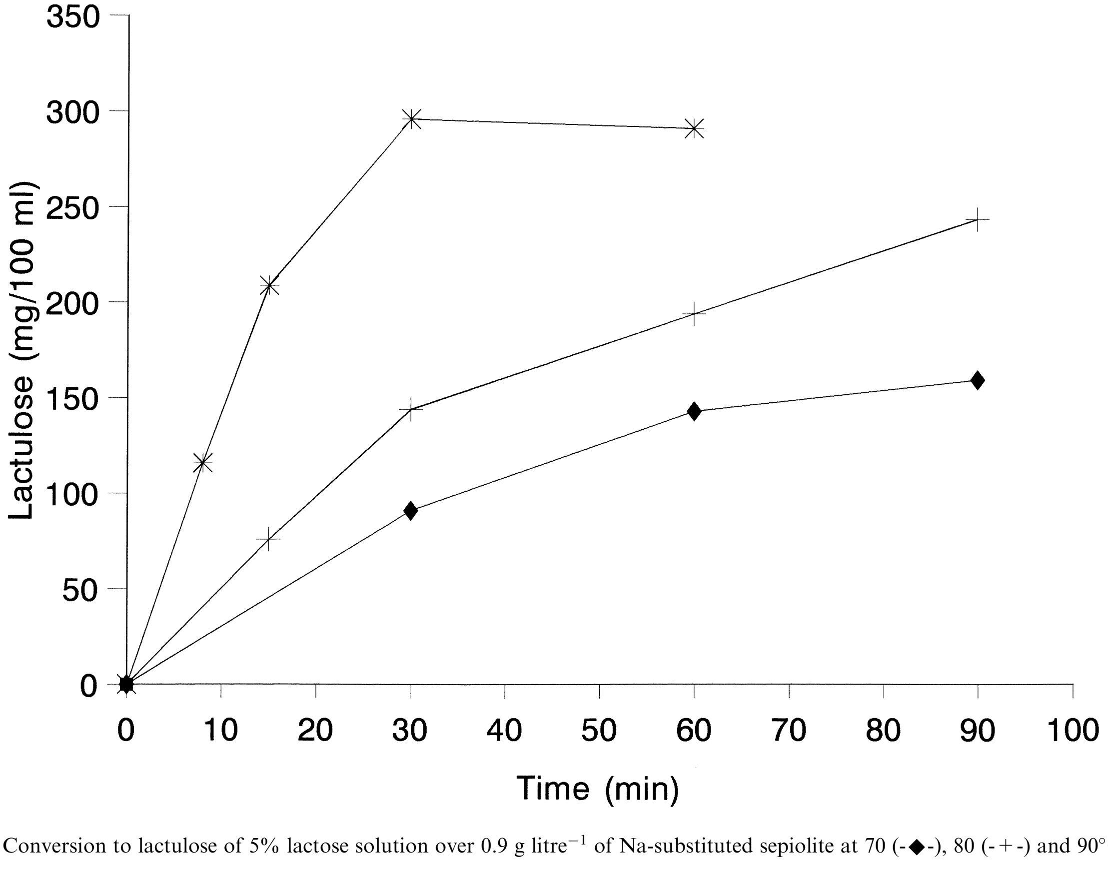

Fig. 3. Conversion to lactulose of 5% lactose solution over 0.9 g litre^{-1} of Na-substituted sepiolite at 70 (-◆-), 80 (-+-) and 90°C (-∗-).

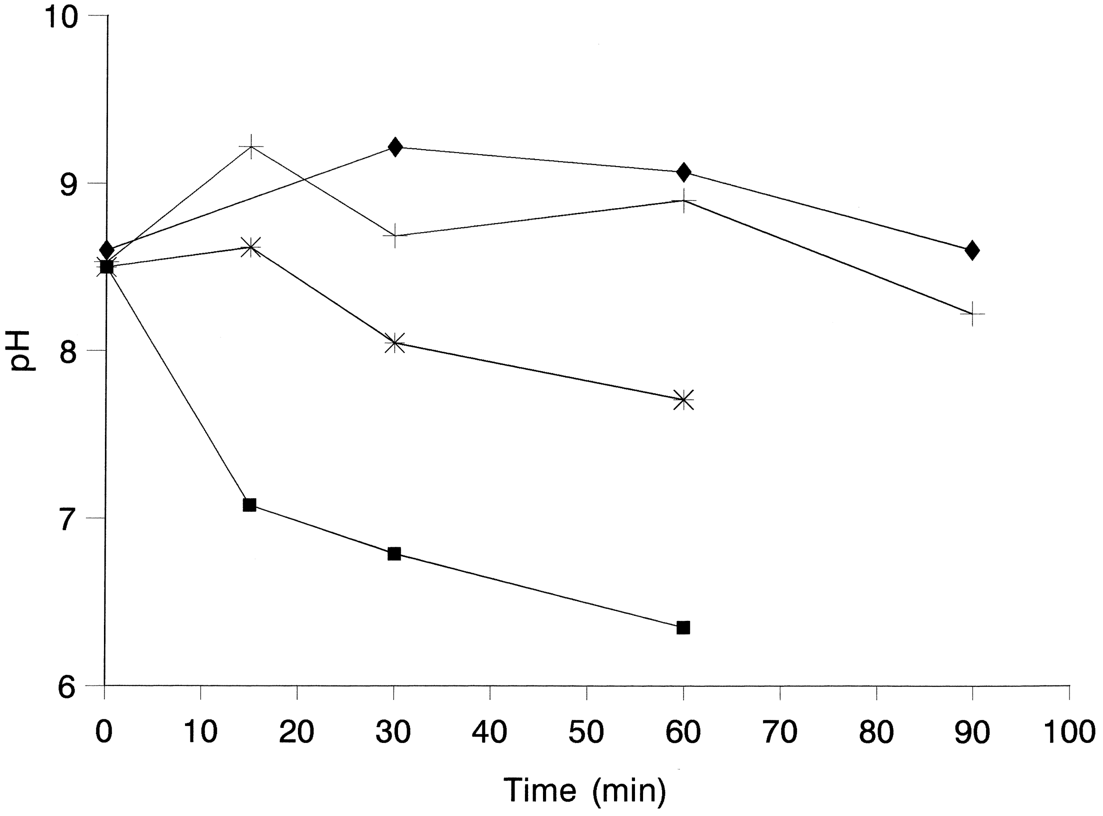

Fig. 4. Evolution of the pH during the isomerization of 5% lactose solution over 0.9 g litre^{-1} Na-substituted sepiolite at 70 (-◆-), 80 (-+-) and 90 (-∗-) and 100°C (-■-).

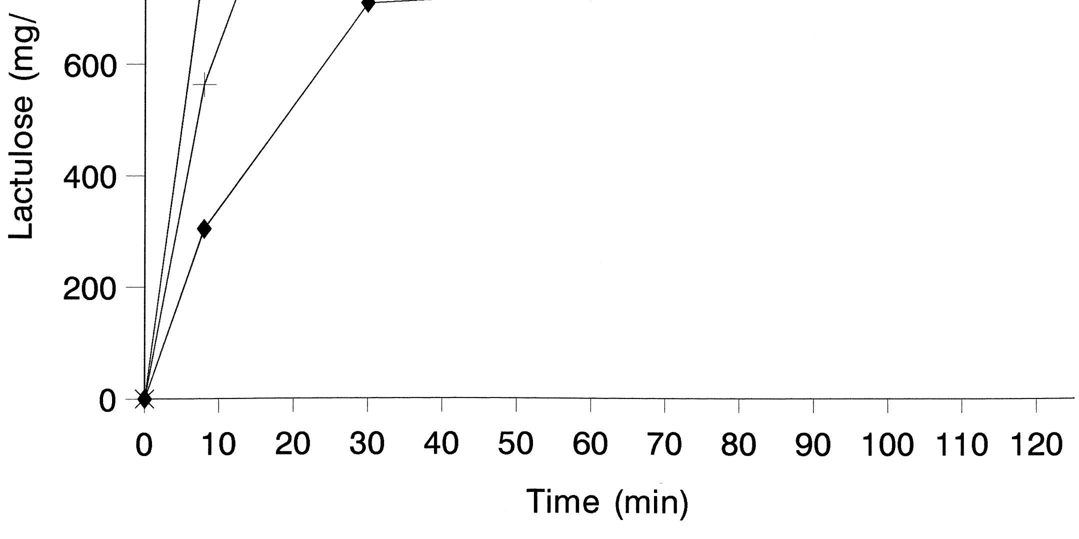

Fig. 5. Conversion of 5% lactose solution to lactulose at 80°C for 30 min over 7.50 (-◆-), 15.0 (-+-) and 30.0 (-∗-) g litre^{-1} of Na-substituted sepiolite.

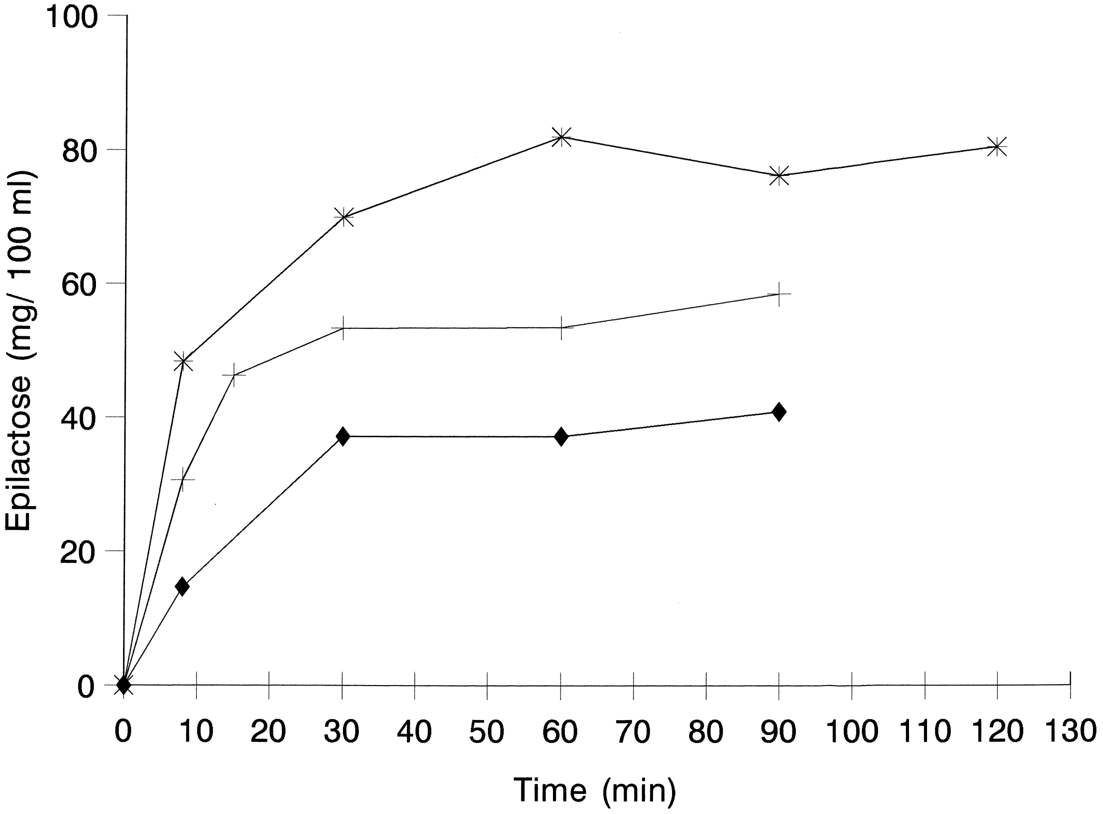

Fig. 6. Conversion of 5% lactose solution to epilactose at 80°C for 30 min over 7.50 (-◆-), 15.0 (-+-) and 30.0 (-∗-) g $litre^{-1}$ of Na-substituted sepiolite.

results clearly demonstrate that the activity exhibited by alkaline-exchanged sepiolites are significantly higher than that of natural sepiolite. Previous study on the use of alkaline-exchanged sepiolites as base catalysts for the Knoevenagel condensation showed the order of activity was Cs > K > Na > Li (Corma & Martín-Aranda, 1991). The observed higher lactulose formation over Li-sepiolite in the present study may be related to its higher content of alkaline metal exchanged.

Isomerization of lactose was investigated over Na-sepiolite at different temperatures and a catalyst loading of 0.9 g $litre^{-1}$. Fig. 3 shows that, at 90°C, the reaction is essentially over after 30 min and at 70–80°C a very large part of the reaction occurs within the first 30 min.

The pH profile of the reaction at 70–100°C is shown in Fig. 4. Upon addition of the catalyst to the lactose solution, the pH rises above 9.0 and then drops as the reaction proceeds. Shukla et al. (1985) attributed the decrease in pH during carbohydrate isomerization over zeolites to dissociative adsorption of water molecules on the surface or to leaching of ionic components from the solid. As is well known, oxidation of carbohydrates in basic media results in the formation of a complex mixture of acids (Isbell, 1973) so, the degradation of lactulose to acidic products must also contribute to the observed decrease in pH.

The effect of catalyst loading in the range 7.50–30.0 g $litre^{-1}$ on isomerization of lactose to lactulose and epilactose at 90°C is shown in Figs. 5 and 6. The conversion of lactose increased with catalyst loading and formation of lactulose and epilactose proceeded through a maximum at a time period of about 60 min.

The ratio lactulose/epilactose formed during lactose isomerization over alkaline-exchanged sepiolites was approximately the same as over natural sepiolite. To obtain a 20% lactose isomerization over natural sepiolite at 100°C, loading of 60 g $litre^{-1}$ is needed (Troyano et al., 1996) Similar conversion is attained at 90°C with alkaline-exchanged sepiolites at a loading of 15 g $litre^{-1}$. These results indicate the usefulness of alkaline-substituted sepiolites for efficient lactose isomerization at moderate temperatures and short periods of time.

Acknowledgements

The authors are thankful to Dr. F. Barba for alkaline metal analyses. Technical assistance by M.J. Rodriguez is also acknowledged.

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