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Alkaline-Substituted Sepiolites as a New Type of Strong Base Catalyst

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Strong base catalysts have been prepared by substituting a part of the Mg^{2+} located at the borders of the channels of sepiolite with alkaline ions. These materials show higher basicity than alkaline X zeolites and are able to catalyze at moderate temperatures the condensation of benzaldehydes with ethyl cyanoacetate, ethyl acetoacetate, and ethyl malonate. The kinetic rate constants obtained indicate that alkaline sepiolites have basic sites with strengths corresponding to $pK_b \leq 13.3$, with most of the sites showing basicities up to $pK_b = 10.7$. © 1991 Academic Press, Inc.

INTRODUCTION

Reactions such as isomerizations, oligomerizations, additions, alkylations, and cyclizations are carried out industrially by using liquid bases as catalysts. The replacement of liquid bases by solid base catalysts would have the advantages of decreasing corrosion and environmental problems, while allowing the separation and recovery of the catalysts. Moreover, for bimolecular reactions, the use of high-surface-area solids as catalysts would increase the probability of reaction by "bringing together" both reactants on the surface of the catalyst.

In this sense, inorganic solids such as rare-earth oxides supported on silica gel (*1*), alkaline earth (*2*) and aluminium (*4, 5*) oxides, xonotlite either alone or with potassium *t*-butoxide (*6*), amines immobilized on silica gel (*7*), and zeolites (*8*) have been used as basic catalysts. It appears from the literature that microporous silicates can be promising catalysts for base-catalyzed reactions.

Sepiolite is a magnesium silicate, the structure of which (*9*) is formed of talc-like ribbons arranged in such a way that the tetrahedral sheet is continuous but inverts in apical directions in adjacent ribbons, generating channels along the *c* axis. The dimensions of the channels are approximately 10.8 × 4.0 Å in a cross section perpendicular to the length of the fiber (*c* axis). The tetrahedral sheet is formed of silicon with only very little substitution by Al^{3+}, and therefore is without acidity. The octahedral sheet is composed mainly of Mg^{2+} with a very small amount of Al^{3+} substitution. The Mg^{2+} ions located at the edges of the octahedral sheet, which form the "walls" of the channels running along the fiber, complete the octahedral coordination by bonding to two molecules of water. These two molecules do not show an acidic character even with respect to NH_3 (*10*).

It appeared to us that base properties could be introduced to this material if the Mg^{2+} at the edges are replaced by alkaline cations. In the present work, Mg^{2+} at the borders have been replaced by Li^+, Na^+, K^+, and Cs^+, and the resultant materials have been used as base catalysts for the condensation of benzaldehyde with ethyl cyanoacetate ($pK \leq 9$), ethyl acetoacetate ($pK = 10.7$), and ethyl malonate ($pK = 13.3$).

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TABLE 1

Chemicals Analysis of the Sepiolite Catalysts (mmol per 100 g of Hydrated Catalyst) and Specific Surface Area (m^2/g)

Sepiolite	Li	Na	K	Cs	Total	BET ($m^2 \cdot g^{-1}$)
Li	140	6	—	—	146	164
Na	—	208	—	—	208	108
K	—	48	57	—	105	165
Cs	—	73	—	51	124	155

EXPERIMENTAL

Materials

All alkaline-exchanged samples were prepared by ion exchange of the sodium form of the sepiolite with the corresponding cation. The sodium form was prepared following the procedure reported in the patent literature (*11*). A natural sepiolite of the "Vallecas" type was used as the starting material and the composition is

$$[Si^{4+}_{11.92}Al^{3+}_{0.08}][Mg^{2+}_{6.98}Fe^{2+}_{0.08}Al^{3+}_{0.54}Fe^{3+}_{0.02}][OH^-]_4 [H_2O]_4[O^=]_{30}K^+_{0.16}Na^+_{0.12}.$$

The Li, K, and Cs forms of sepiolite were prepared by exchanging the Na^+ in the sodium form of sepiolite, in a batch reactor in a stirred solution of the desired alkaline cation, at 353 K and a solid to liquid ratio of 10, for 1 h. After the ion exchange, the samples were washed and dried at 388 K for 15 h. No further activation of the sample was carried out before use. The cation content on the solid was obtained by destroying the samples in a hydrochloric solution and analyzing the alkaline cation content in the liquid by atomic absorption and emission. The results obtained together with the BET surface area of the catalysts are given in Table 1.

A Mg–Al hydrotalcite was prepared by mixing two solutions, A and B, at 60 ml$\cdot$ h^{-1} for 4 h under stirring. Solution A was prepared by disolving $Mg(NO_3)_2$ and $Al(NO_3)_3$ in distilled water until the solution was 1.5 *M* in Mg + Al, with an Al/(Al + Mg) atomic ratio equal to 0.25.

Solution B was prepared by dissolving in water Na_2CO_3 and NaOH, in such a way that when both solutions A and B were mixed the following ratios were achieved:

$$CO_3 = /(Al + Mg) = 0.666 \text{ and } OH^-/(Al + Mg) = 2.25.$$

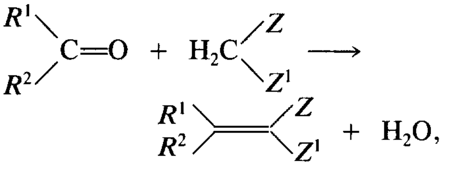
The final pH achieved after A and B were mixed was 13.0. The resultant gel was heated in an autoclave at 473K for 18 h, and then filtrated and washed until the pH of the wash water was 7.0. After drying at 353K for 12 h, the hydrotalcite was calcined at 723K for 18 h. The BET surface area of the results catalyst was 175 m^2 g^{-1}.

Reaction Procedure

An equimolar mixture of benzaldehyde (14.0 mmol) and either ethyl cyanoacetate or ethyl malonate at the desired reaction temperature was heated, while stirring, in a batch reactor and in the absence of a solvent. Then, 1 or 10 wt% of the catalyst with respect to the total amount of reactants was added depending on whether ethyl cyanoacetate or ethyl malonate, respectively, was used. Samples of the products were taken at different reaction times, as given in Fig. 1, and analyzed by GLC and ^1H NMR. The NMR analysis was carried out in a 90-MHz Varian spectrophotometer using $CDCl_3$ as solvent and TMS as reference standard.

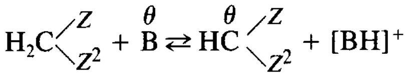
RESULTS AND DISCUSSION

The Knoevenagel condensation of aldehydes or ketones with molecules containing activated methylene groups to form olefines is a reaction typically catalyzed by bases,

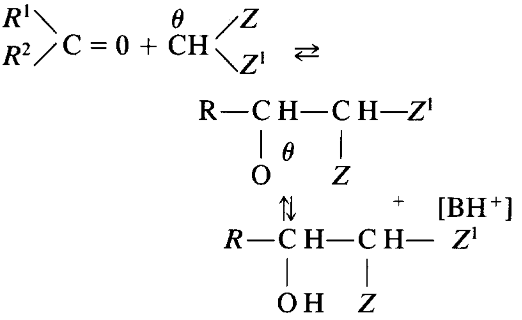


[1]

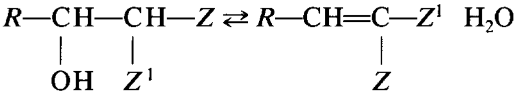
where R^1 and R^2 can be aliphatics, aromatics, or H groups. Z and Z^1 can be groups such as CN, CO_2Et, CO_2H, and $CONH_2$. The accepted mechanism for this type of reaction involves, as a first step, the abstraction of a proton of the methylene group by the base with the formation of the corresponding carbanion.



The formed carbanion attacks the carbonyl group of the aldehyde, giving the corresponding intermediate alcohol of the condensed product.



In a last step, water is removed and the olefin formed:



$$\underset{OH}{R\text{—}CH}\text{—}\underset{Z^1}{CH}\text{—}Z \rightleftarrows R\text{—}CH{=}\underset{Z}{C}\text{—}Z^1 \quad H_2O$$

Kinetically, it has been found (*12*) that, depending on whether the controlling step is the proton abstraction or the condensation step, a first- or a second-order kinetic equation, respectively, applies. This type of reaction not only is of practical interest for the preparation of fine chemicals such as nifedipine and nitrendipine (*13*), which are used as antihypertensives and calcium antagonists, but also can be used as a test reaction for base catalysts. Indeed, by changing the electrodonating ability of the groups Z and Z^1 in reaction [1], the abstraction of the proton will be more or less difficult, and therefore a catalyst with stronger or less strong basic sites will be needed. If this is so, it should be possible to correlate the basicity of the catalyst with the pK of the methylenic group. Following this idea we have chosen as methylenic compounds ethyl cyanoacetate, ethyl acetoacetate, and ethyl malonate, which have p$K < 9, < 10.7$ and < 13.3, respectively.

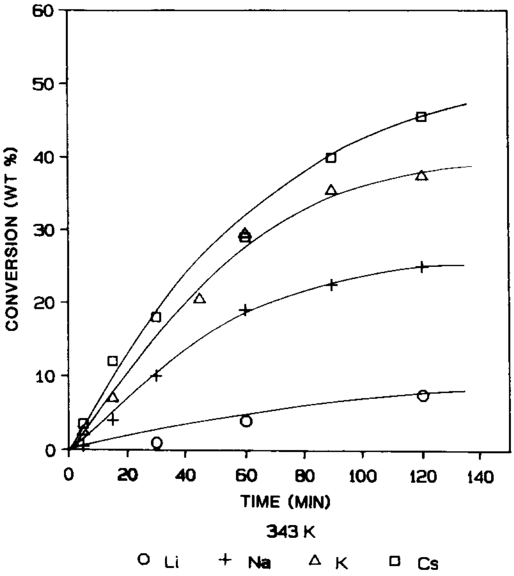


FIG. 1. Condensation of benzaldehyde (14 mmol) and ethyl cyanoacetate (14 mmol) at 343 K using alkaline sepiolites (0.031 g).

For liquid phase reactions catalyzed by solid catalysts, special care should be taken to avoid diffusion limitations. In this work, and to avoid external and internal diffusion, a series of experiments using benzaldehyde and ethyl cyanoacetate as reactants and Na and Cs sepiolite as catalysts was carried out by changing the stirring speed (1000 and 3500 rpm) and the catalyst particle size (≤ 0.074; ≤ 0.14; ≤ 0.25 mm in diameter). The results obtained indicate that, in this

TABLE 2

Condensation of Benzaldehyde and Ethyl Cyanoacetate (14 mmol) at 323, 343, and 363 K Using Alkaline Sepiolites (0.031 g)

Catalyst	T (K)	Yield(%)[a,b]	K[c]	K[d]	E_a[e]
Sep. Li	323	3	0.1	6.8	
	343	8	0.3	27.4	72
	363	28	0.9	109.0	
Sep. Na	323	15	0.5	24.0	
	343	25	1.1	57.7	51
	363	57	4.5	235.6	
Sep. K	323	25	0.7	114.3	
	343	38	1.3	209.6	32
	363	58	2.8	438.1	
Sep. Cs	323	28	0.9	112.9	
	343	46	1.8	233.9	39
	363	68	4.6	572.6	

[a] Reaction time 2 h.

[b] Knoevenagel condensation product. 100% selectivity.

[c] Kinetics rate constant (mol · s^{-1} · m^2) × 10^{-3}.

[d] Kinetic rate constant (mol · s^{-1} · mmol alkaline metals) × 10^{-3}.

[e] Activation energies (KJ · mol^{-1}).

range of conditions, the reaction is controlled by neither external nor internal diffusion. Thus, we can safely compare the activity and selectivity of the different sepiolite catalysts under these reaction conditions.

The yields of olefin obtained during the condensation of benzaldehyde (14 mmol) with ethyl cyanoacetate (14 mmol) in the presence of Li, Na, K, and Cs sepiolites at 323, 343, and 363 K are given in Table 2. No hydroxyl intermediates were detected in the reaction media. From these results it becomes apparent that the order of activity is Cs > K > Na > Li. To quantify the activity of the catalysts, the conversion at different reaction times (Fig. 1) has been fitted to a first-order kinetic expression (abstraction of the proton as the controlling step) and to a second-order rate expression (the condensation itself as the controlling step). Very good correlations ($r \geq 0.99$) have been obtained with both kinetic expressions, but they are slightly better with the second-order model. Therefore, the kinetic rate constants given in Table 2 have been calculated on the basis of a second-order model. This result confirms the order of activity given above as a function of the cation introduced at the borders of the octahedral sheet of the sepiolite and indicates that the anionic character of the framework increases when the charge density on the cation decreases. This conclusion can also be reached if one calculates the Sanderson electronegativity (*14*) of the different sepiolites. According to the compositions given in Table 1, the values obtained are 3.95, 3.88, 3.86, and 3.84 for Li, Na, K, and Cs sepiolites, respectively. The lower the Sanderson electronegativity, the higher the density of negative charge on the oxygens at the border and, therefore, the more basic the sepiolite. However, it should be considered that for sepiolite with tetrahedral and octahedral sheets, the Sanderson electronegativity could be used, at the most, only to compare homologous series of sepiolites.

The activation energy has been calculated

TABLE 3

Kinetic Rate Constants for the Condensation of Benzaldehyde (9.4 mmol) with Ethyl Acetoacetate (9.4 mmol) and Benzaldehyde (7 mmol) with Ethyl Malonate (7 mmol) Using Cesium-Exchanged Sepiolite (0.022 and 0.19 g, Respectively)

Methylenic compound	T(K)	K^a	K^b
Ethyl acetoacetate	413	1.4	177.4
	438	14.1	1766.6
Ethyl malonate	403	0.1	14.4
	423	0.3	33.1
	443	0.4	46.0

[a] Kinetic rate constant (mol · s^{-1} · m^2) × 10^{-3}.

[b] Kinetic rate constant (mol · s^{-1} · mmol alkaline metals) × 10^{-3}.

by means of the Arrhenius equation (Table 2) and the kinetic rate constants obtained at 323, 343, and 363 K. The values obtained are typical of a chemical process and, in general, it can be said that the activation energy for the condensation of benzaldehyde and ethyl cyanoacetate decreases with an increase in the radius of the cation, i.e., with increasing strength of the base catalyst.

The condensation of benzaldehyde with ethyl acetoacetate and ethyl malonate has been carried out on Cs sepiolite at temperatures higher than those with the ethyl cyanoacetate in order to achieve high conversions. The rate constants obtained (Table 3) indicate that the reaction becomes progressively slower with increases in the pK of the methylenic activated reactant. The activation energy is similar for all the compounds. Using the Arrhenius equation and the activation energy values, the rate constants at 423 K of reaction temperature are calculated per unit surface area of the catalyst and unit volume of reactor for the three reactants. It is found that the kinetic rate constant for the ethyl cyanoacetate is about 4 times higher

TABLE 4

Activity of Pyridine and Piperidine as Catalysts for the Condensation of Benzaldehyde and Ethyl Cyanoacetate and Ethyl Acetoacetate

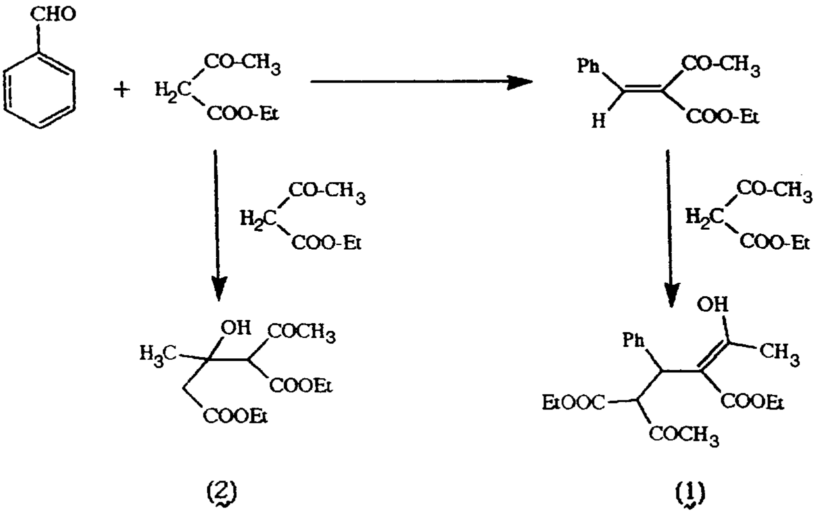
Catalysts	Z	T (K)	Time (min)	Conv. (%)[a]	Other prod. (%)
Pyridine	CN	323	15	0	—
			60	1	—
			300	4	—
Pyridine	CN	343	30	2	—
			60	3	—
			360	15	—
Pyridine	CN	363	5	2	—
			60	10	—
			120	17	—
Piperidine	CN	323	5	80	—
			15	92	—
Piperidine	$COCH_3$	438	15	49	4
			30	46	8
			45	44	12
			60	40	14
Piperidine	$COCH_3$	413	180	5	50

[a] Product of Knoevenagel condensation.

than that for ethyl acetoacetate and about 30 times higher than that for ethyl malonatae condensation. These results would indicate that alkaline sepiolites show most of their basicity at p$K_b \leq 9.0$, with a sensible number of basic sites with pK between 9 and 10.7 and very little sites with pK_b between 10.7 and 13.3. As we did previously (*8*) with base zeolites we attempted to analyze the basicity of sepiolites on the basis of the ir spectra of pyrrole adsorption. In this case, only a broad band at ≈3430 cm^{-1} corresponding to physisorbed pyrrole was observed and it was not possible to use this technique to measure the relative basicity of sepiolite catalysts.

To compare the basicity of the sepiolites with that of other base catalysts, the condensation of benzaldehyde with ethyl cyanoacetate was carried out in the presence of pyridine (pK_b = 8.8) and piperidine (pK_b = 11.12). The amounts of pyridine and piperidine used as catalyst were the same as the number of equivalents of cations present in the sepiolite in similar experiments. The results presented in Table 4 show that pyridine is less active than sepiolites, while piperidine is more active than any of the sepiolites studied.

With regard to the condensation of benzaldehyde with ethyl acetoacetate using piperidine as catalyst, it should be noted that the activity is much higher than the activity of sepiolites, but its selectivity for the Knoevenagel condensation is much lower (Table 4). The two main undesired products obtained (**1**) and (**2**) were identified by mass spectroscopy and have been produced through the following reactions:



In the case of sepiolites, the product (**1**) formed through a Michael-type reaction was not observed, probably due to geometrical constraints to form the bulky product. This was not observed when zeolites were used as catalysts. On the other hand, the formation of product (**2**) through an aldolic condensation on a ketonic group requires a relatively stronger basic site. Then if catalysts with mild basicity, such as sepiolites and zeolites, are used, such reaction is avoided.

When the activity of sepiolites is compared (Fig. 2) with the activities of Faujasite zeolites (*8*) and hydrotalcite (*15*), the former are about 3 times more active than X zeolites and about 50 times more active than Y zeo-

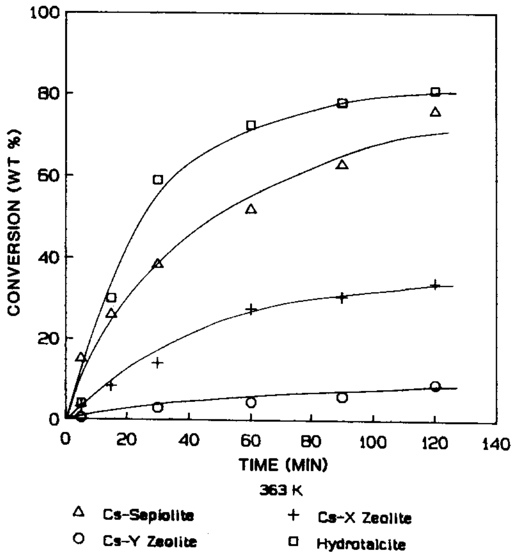


FIG. 2. Condensation of benzaldehyde (14 mmol) and ethyl cyanoacetate (14 mmol) at 363 K using Cs sepiolite, Cs–X zeolite, Cs–Y zeolite, and hydrotalcite (0.031 g).

lites, while the activation energies are similar for sepiolite and X zeolite and sensibly lower than those for Y zeolite. On the other hand, the activity of a thermally activated layered hydroxide, such as hydrotalcite, which gives a fairly strong base (*16*), is more active than Cs sepiolite for the Knoevenagel reactions studied here (see, for instance, the results in Fig. 2). However, in agreement with the explanation given above for the occurrence of the aldolic condensation reaction, stronger base catalysts are less selective than milder catalysts such as zeolites and sepiolites for Knoevenagel reactions. Indeed, when hydrotalcite is used as a catalyst to condense benzaldehyde with ethyl acetoacetate, the second reactant can condense with itself to give the product (**2**). In other words, alkaline sepiolites, first reported here, are microcrystalline base catalysts, thermally and chemically stable and with stronger basicity than zeolites. These materials very selectively catalyze the Knoevenagel-type condensation.

TABLE 5

Kinetic Rate Constants for the Condensation of Benzaldehyde and Ethyl Cyanoacetate on Alkaline Sepiolites, Alkaline X and Y Zeolites, and Hydrotalcites at 363 K

Catalyst	K^a	K^b
Sep. Li	0.900	109.0
Sep. Na	4.500	235.6
Sep. K	2.800	438.1
Sep. Cs	4.600	572.6
Z X Li	0.030	5×10^{-3}
Z X Na	0.170	24×10^{-3}
Z X K	0.240	28×10^{-3}
Z X Cs	0.220	40×10^{-3}
Z Y Li	0.011	2×10^{-3}
Z Y Na	0.015	3×10^{-3}
Z Y K	0.015	4×10^{-3}
Z Y Cs	0.018	5×10^{-3}
Hydrotalcite	289.000	—

[a] Kinetic rate constant (mol $s^{-1} \cdot m^2$).

[b] Kinetic rate constant (mol s^{-1} · mmol alkaline metals).

CONCLUSIONS

It is possible to prepare stable base catalysts by introducing alkaline cations at the borders of the octahedral sheets of sepiolites. These catalysts are active and selective catalysts for carrying out condensation of aldehydes with molecules containing activated hydrogens (Knoevenagel reaction). These materials have basic sites of strengths corresponding to $pK_b \leq 13.3$, and are more active than alkaline-exchanged Faujasite zeolites but less active than hydrotalcite.

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