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Determination of Base Properties of Hydrotalcites: Condensation of Benzaldehyde with Ethyl Acetoacetate

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By carrying out the condensation of benzaldehyde with activated methylenic groups with different pK values, in the presence of a Mg–Al hydrotalcite catalyst, it has been found that this material shows basic sites with pK values up to 16.5. However, most of the basic sites show pK values in the range 10.7–13.3. In the use of zeolites as catalysts, the only reaction observed was Knoevenagel condensation, while on calcined hydrotalcite other reactions, the Michael-type addition and the Claisen condensation, also occur. These reactions require stronger basicities than the Knoevenagel condensation to occur. By carrying out the Knoevenagel condensation, using methylenic groups of different pK values, in the presence of increasing amounts of benzoic acid, it is possible to measure the total amount of basic sites and their strength distribution as determined under reaction conditions. By increasing the Mg/Al ratio in the hydrotalcite, the number of basic sites with $9.0 \leq \mathrm{p}K \leq 13.3$ increases, whereas the amount of basic sites within $13.3 \leq \mathrm{p}K \leq 16.5$ decreases.

INTRODUCTION

Basic solids and base-catalyzed reactions have received a great deal of attention in recent years because they constitute an unexplored field that offers possibilities for selectively catalyzing reactions involved in the production of fine chemicals and commodities (*1–5*).

Besides the classic low-surface-area alkaline earth solids and the strong metal alkaline catalysts, researchers have looked to milder high-surface-area basic compounds, which can combine base catalysis and, in some cases, shape selectivity. Among those, zeolites (*6*), sepiolites (*7*), organic resins (*8*), and hydrotalcites (*9*) can be prepared in a wide range of basic strengths; therefore, depending on the basic strength needed, the appropriate catalyst can be selected to catalyze more selectively the desired reaction.

Among the high-surface-area base solid catalysts named above, hydrotalcites present the strongest basicity. However, it becomes difficult to measure the basic strength distribution with existing methods. Techniques such as titration with indicators (*10*), CO_2 (*11*), and benzoic acid (*12*) and spectroscopic techniques (*13*) present, besides their particular limitations, the overall inconvenience that they are indirect measurements of the basicity, since they are carried out under experimental conditions far from real reaction conditions.

We recently proposed that, in base-catalyzed reactions where the first step is the abstraction of a proton by the catalyst, one should be able to measure not only the total amount of basic sites but also the basic strength distribution, by using, as reactants, molecules with different pK_a values, i.e., molecules presenting different well-established difficulties for proton abstraction (*6*).

We have used this technique here to study a very interesting basic type of materials such as calcined hydrotalcites. The general composition of these materials is $M_a^{2+}M_b^{3+}(\mathrm{OH})_{2a+2b}\,(X^{n-})_{b/n}\cdot x\mathrm{H_2O}$ and they are formed by sheets of $M^{3+}(\mathrm{OH})_6$ and

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$M^{2+}(OH)_6$ octahedra. The presence of the trivalent M^{3+} ions generates a net positive charge on the sheet which is balanced by interlayer anions. Hydrotalcite-type materials become active as solid base catalysts when heated at about 673 K to give dehydrated and dehydroxylated mixed oxides (*9*). It has been suggested that the active sites are the low-coordinated OH^{2-} situated in the borders and defect sites of the mixed oxide structure (*14*).

The relative broad range of strengths in the surface basic sites of thermally treated hydrotalcites suggests that a wide variety of base-catalyzed reactions can be promoted by these materials.

In this work, we have studied the catalytic activity and selectivity of a hydrotalcite for the Knoevenagel condensation of benzaldehyde with activated methylenic compounds, where the abstraction of the proton in the activated methylenes require different basicities.

EXPERIMENTAL

Materials

Two Mg–Al hydrotalcites were prepared by mixing two solutions, A and B, at the same rate of addition (60 ml h^{-1}) for 4 h, while stirring. Solution A was prepared by dissolving $Mg(NO_3)_2$ and $Al(NO_3)_3$ in distilled water until the solution was 1.5 *M* in Mg + Al, with Al/(Al + Mg) atomic ratios equal to 0.25 and 0.33.

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:

$$CO_3^{2-}/(Al + Mg) = 0.666$$

$$OH^-/(Al + Mg) = 2.25 \quad \text{and} \quad 2.33.$$

The final pH achieved after mixing A and B was 13.0. The resultant gel was heated in an autoclave at 473 K for 18 h, and then filtered and washed until the pH of the washing waters was 7.0. After drying at 353 K for 12 h, the hydrotalcites were calcined at 723 K for 18 h. The characteristics of the resultant hydrotalcite catalysts are given in Table 1. The XRD pattern of the synthesized samples shows only the diffraction peaks corresponding to hydrotalcite (HT). Meanwhile, the calcined solids show a diffuse MgO pattern. Both synthesized hydrotalcites are in the form of hexagonal platelet-shaped crystallites, with crystal size in the range 250–500 nm. After the calcination procedure no changes were observed in the morphology.

In the synthesized samples, all aluminum is within an octahedral coordination, as shown by the presence of only one single Al^{27} MAS NMR peak located at 9 ppm. However, after calcination both Al^{IV} (72 ppm) and Al^{VI} (16 ppm) are present. The ratio $Al^{IV}/(Al^{IV} + Al^{VI})$ calculated from the integrated intensities of the corresponding lines is 0.33 for both HT-1 and HT-2 samples.

Reaction Procedure

An equimolar solution of benzaldehyde and ethyl acetoacetate without solvent was magnetically stirred, while heating to the reaction temperature in a silicone bath. Then, 1 wt% of the hydrotalcite catalysts was added and the reaction started. Samples were taken periodically, and the evolution of the reaction between 5 and 300 min was followed by gas–liquid chromatography, on a 25-m phenylsilicone capillary column, and mass spectroscopy. ^1H NMR spectra of the products were obtained on a 90-MHz spectrometer using chloroform as solvent and tetramethylsilane as reference.

RESULTS AND DISCUSSION

Under these experimental conditions several reaction products were obtained (Scheme 1). When the yield of each one of those is plotted versus the total conversion (Fig. 1) it can be seen that the product from the Knoevenagel condensation, **1**, which is in the majority, behaves as a primary unstable product, whereas **2** and **3** are secondary and stable products. Product **4** appears as a primary and stable product. The three isomers, **7a, b, and c,** are primary and stable

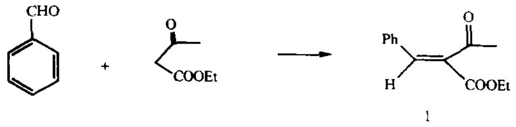
TABLE 1

Chemical Analysis and Surface Area of Calcined Hydrotalcites

Sample	MgO (wt%)	Al_2O_3 (wt%)	Al/(Al + Mg)	Surface area (m^2 g^{-1})
HT-1	70.4	29.5	0.25	175
HT-2	66.1	33.8	0.30	173

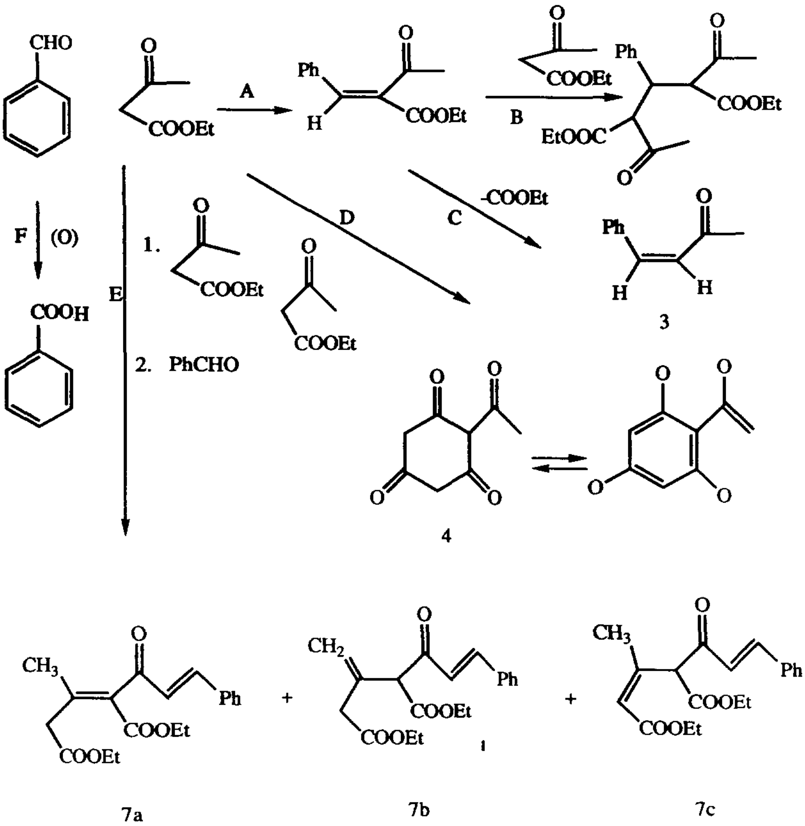
products. Finally, benzoic acid is formed as a primary and unstable product.

The first thing to be remarked is that calcined hydrotalcite is less selective than either zeolites (6) or sepiolites (7) for the Knoevenagel reaction, since on these materials, only product **1** was detected. This is a first indication that hydrotalcites show a wider range of basic strengths than the aforementioned silicates.



(1)

The fact that the typical Knoevenagel product is unstable under the present experimental conditions, while **2** appears as a secondary stable product, could be explained



SCHEME 1. (A) Knoevenagel condensation. (B) Michael addition. (C) Decarboxylation. (D) Claisen condensation and cyclization. (E) Aldolic condensation. (F) Oxidation of benzaldehyde.

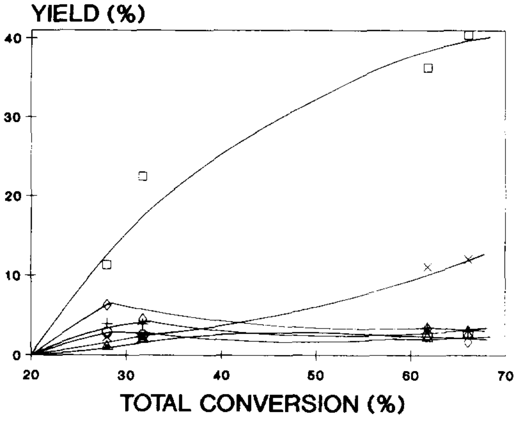
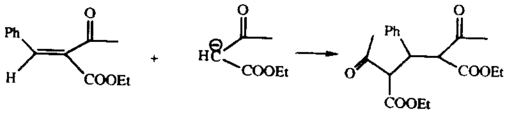


FIG. 1. Condensation of benzaldehyde and ethyl acetoacetate selectivity to the reaction products at 393 K on hydrotalcite as catalyst. (□) product **1**, (×) product **2**, (■) product **3**, (○) product **4**, (◇) products **7a–c**, (+) benzoic acid, (△) product.

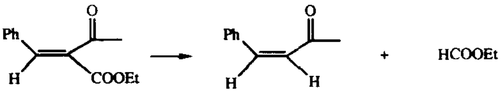
by considering that product **1** can react with a second molecule of ethyl acetoacetate following a Michael-type addition:



2

(2)

Moreover, product **3** could be formed from product **1** by decarboxylation:

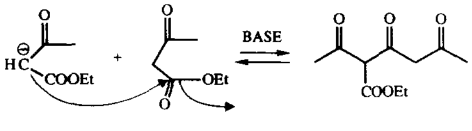


3

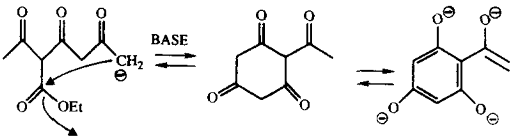
(3)

This reaction explains the secondary character of product **3**, while it contributes to the unstability shown by product **1**.

Product **4** can be formed by two consecutive Claisen condensations and cyclizations of two molecules of ethyl acetoacetate:



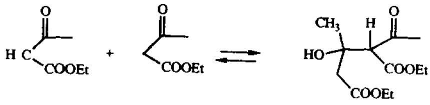
(4)



4

(5)

Aldolic condensation of two molecules of ethyl acetoacetate, followed by a condensation with benzaldehyde, can also occur, and is responsible for some of the observed products (**7a–c**).



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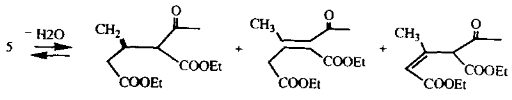
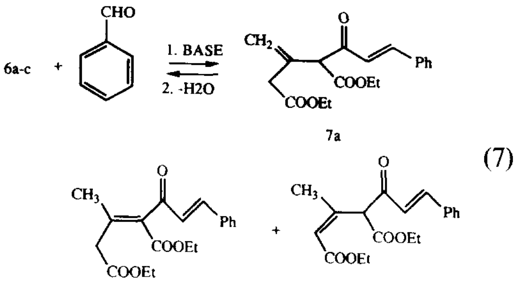


6a 6b 6c

(6)



7a

(7)

7b 7c

Finally, benzoic acid can be formed by the oxidation of benzaldehyde by the oxygen present in the reactor.

On these bases, a reaction network for the condensation of benzaldehyde and ethyl acetoacetate on a hydrotalcite catalyst can be written, and it is given in Scheme 1.

The formation of products **2** and **3** through reactions (2) and (3) was checked by reacting, on a separate batch, product **1** with ethyl acetoacetate under the same experimental conditions. High yields of **2** and **3** were observed.

When ethyl acetoacetate, alone, was

placed under reaction conditions in the presence of calcined hydrotalcite, products **5** and **6** were observed. Then, if benzaldehyde was added, product **7** appeared.

The formation of benzoic acid by oxidation of benzaldehyde was checked by carrying out the Knoevenagel condensation as before, but in a N_2 atmosphere. Under these conditions the formation of benzoic acid was practically negligible.

When the condensation of benzaldehyde with ethyl acetoacetate was carried out on zeolites and sepiolites, only product **1** was observed (*6, 7*). Meanwhile, it was shown that those silicates present most of the basic sites with $pK \leq 10.7$ and a quite small number of sites in the range $10.7 \leq pK < 13.3$. Those basicities, although strong enough to carry out the reaction, are not basic enough to produce the aldolic condensation and the Michael-type addition. Indeed, if the Knoevenagel reaction is carried out in the presence of pyridine ($pK \leq 9$), only product **1** is detected, while if the same reaction is carried out with piperidine as catalyst ($pK = 11.2$), the Michael addition and aldolic condensation products are also formed. In the case of hydrotalcites both reactions occur, indicating that, on this material, the basicity is shifted to stronger values with sites with pK of at least 10.7.

Basic Strength Distribution in Calcined Hydrotalcite

To study the base strength distribution of these materials, the calcined hydrotalcites were used to catalyze Knoevenagel reactions with benzaldehyde and methylenic groups with different pK, i.e., ethyl cyanoacetate ($pK \leq 9$), ethyl malonate ($pK = 13.3$), and ethyl bromoacetate ($pK = 16.5$). The conversion was followed at different reaction times, and the results for sample HT-1 are given in Fig. 2.

By fitting those results to a second-order kinetic equation (*4*), the kinetic rate constants were calculated for both samples and the results are presented in Table 2. When the results are compared with those obtained previously on other solid base catalysts (Figs. 3 and 4), it can be seen that, unlike zeolite and sepiolites, calcined hydrotalcite contains basic sites of pK_a values up to 16.5. However, most of its basic sites have $10.7 \leq pK \leq 13.3$, and only few of them show strengths $13.3 \leq pK \leq 16.5$. Results from Table 2 also indicate that by increasing the Mg/Al ratio in the hydrotalcite the total amount of basic sites increases but the proportion of

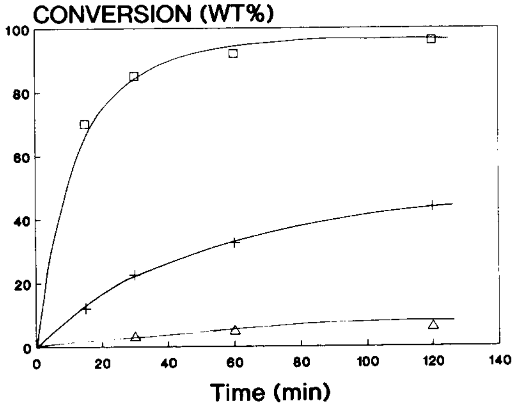


FIG. 2. Condensation of equimolar amounts of benzaldehyde and (□) ethyl cyanoacetate, (+) ethyl malonate, and (△) ethyl bromoacetate at 403 K using 1, 10, and 10 wt% of hydrotalcite, respectively.

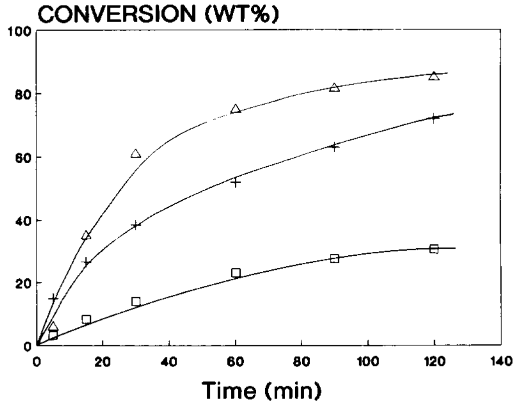


FIG. 3. Condensation of benzaldehyde (14 mmol) and ethyl cyanoacetate (14 mmol) at 393 K using (△) hydrotalcite, (+) Cs-sepiolite, and (□) Cs-X zeolite (0.031 g).

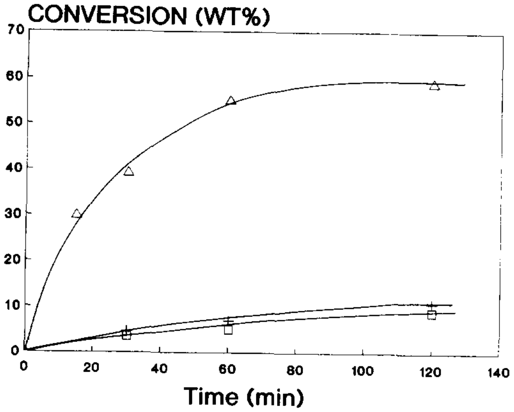


FIG. 4. Condensation of benzaldehyde (7 mmol) and ethyl malonate (7 mmol) at 443 K using (△) hydrotalcite, (+) Cs-sepiolite, and (□) Cs-X zeolite (0.19 g).

stronger basic sites, i.e., those catalyzing the condensation of benzaldehyde and ethylbromoacetate, decreases.

It must be remarked that, in the condensation of benzaldehyde and ethyl bromoacetate, the product obtained is not that corresponding to the Knoevenagel condensation, but the corresponding epoxide formed by a Darzens reaction and reaction products from benzoic acid and ethylbromoacetate (Scheme 2). Formation of the epoxide is favored in this case because the intermediate halohydrin **8** reacts in a SN_2-type displacement with the bromide ion, as the leaving group, to afford the corresponding Darzens glycidic ester **9**.

Catalyst Decay due to the Formation of Benzoic Acid: Influence on Selectivity

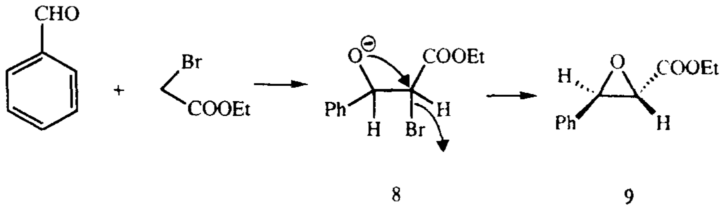
It was mentioned above that benzaldehyde is oxidized to benzoic acid during the condensation reaction when carried out in the presence of air. The benzoic acid, when formed, can adsorb on the catalyst, poisoning the basic sites. To discuss this effect, the condensation of benzaldehyde (9.4 mmol) and ethyl acetoacetate (9.4 mmol) was carried out in the presence of calcined hydrotalcite (0.022 g) at 393 K. Benzoic acid (3 × 12 mmol) was added to the reactor at 0, 20, and 35 min of reaction. Results from Table 3 clearly show that benzoic acid is indeed a strong poison for the reaction. Meanwhile, if the selectivities of the different products obtained during this experiment are com-

TABLE 2

Kinetic Rate Constants for the Condensation of Benzaldehyde (14 mmol) with Ethyl Cyanoacetate (14 mmol), Benzaldehyde (7 mmol) with Ethyl Malonate (7 mmol), and Benzaldehyde (7 mmol) with Ethyl Bromoacetate (7 mmol) on HT-1 (0.031, 0.190, and 0.192 g, Respectively)

Methylenic compound	T (K)	K	
		(mol s^{-1} g^{-1}) × 10^{-4}	(mol s^{-1} g^{-1} m^{-2}) × 10^{-4}
Ethyl cyanoacetate	343	1,258.43	7.27[a]
	343	6,186.0	35.350
	363	15,698.0	89.700
	393	49,079.0	280.450
Ethyl malonate	403	341.76	1.975[a]
	403	339.00	1.937
	423	1,543.9	8.823
	443	1,380.53	7.888
Ethyl bromoacetate	363	10.30	0.060[a]
	363	6.77	0.038
	383	13.91	0.079
	403	41.92	0.239

[a] HT-2 catalyst sample.



SCHEME 2

pared with those obtained in analogous experiments without benzoic acid (Table 4), it is seen that the reactions more efficiently poisoned are the most demanding, such as the Michael addition and the aldolic condensation. The Knoevenagel condensation is much less affected by the presence of benzoic acid. These results indicate that the acid poisons the stronger basic sites first.

If one keeps adding benzoic acid, all the active sites become poisoned, and the Knoevenagel condensation even stops. At this moment, and assuming that one acid molecule poisons one basic site, it is possible to calculate the millimoles of basic sites per unit surface area present on the calcined hydrotalcite. The value obtained was 12 mmol basic site m^{-2}. This value is of the same order as that found by Miyata (*15*) for a calcined hydrotalcite with a similar composition, but using Hammet indicators.

CONCLUSIONS

When ethyl acetoacetate is reacted with benzaldehyde on a calcined Mg–Al hydrotalcite, besides the Knoevenagel condensation, other more demanding reactions, i.e., Michael-type addition, Claisen condensation, cyclization of two molecules of ethyl acetoacetate, and aldolic condensation, also occur. None of these reactions took place when benzaldehyde and ethyl acetoacetate

TABLE 3

Condensation of Benzaldehyde (9.4 mmol) with Ethyl Acetoacetate (9.4 mmol) on HT-1 at 393 K, Adding Benzoic Acid (2 wt%) Periodically

t (min)	Conversion (%)	*a*	*b*	*c*	*d*	*e*	*f*	*g*
5	10.33	5.33	0.22	0.03	0.06	0.70	3.70	0.04
10	10.93	4.80	0.20	0.04	0.09	0.70	4.90	0.07
20	15.00	6.40	0.10	0.11	0.11	1.30	6.80	0.07
25	15.02	6.30	0.10	0.17	0.23	1.40	6.40	0.20
30	12.50	7.00	0.20	0.19	0.31	1.50	3.00	0.22
35	14.30	7.30	0.20	0.22	0.49	1.60	4.20	0.24
60	18.50	9.60	0.30	1.10	0.52	3.00	3.60	0.28
65	18.20	7.50	0.30	1.13	0.53	3.22	4.50	0.33
120	35.90	11.50	0.50	7.51	1.70	6.50	6.40	0.83

[a] Knoevenagel condensation product **1** (%).
[b] Knoevenagel condensation product decarboxylated **3** (%).
[c] Products **7a, b,** and **c** (%).
[d] Product **2** (%).
[e] Benzoic acid (%).
[f] Product **4** (%).
[g] Other products (%).

TABLE 4

Condensation of Benzaldehyde (9.4 mmol) with Ethyl Acetoacetate (9.4 mmol) on HT-1 at 393 K

t (min)	Conversion (%)	*a*	*b*	*c*	*d*	*e*	*f*	*g*
15	32.35	7.09	0.805	9.90	4.22	3.65	3.00	2.13
30	29.10	6.30	1.05	11.31	2.29	3.97	2.85	1.13
60	31.72	5.14	1.31	12.70	1.30	4.01	2.50	1.80
120	31.76	4.51	2.07	22.40	2.23	3.91	2.51	2.03
180	61.80	3.43	3.24	36.30	11.11	3.52	2.55	2.26
300	66.06	1.71	3.40	40.41	12.07	3.07	2.77	2.63

[a] Knoevenagel condensation product **1** (%).
[b] Knoevenagel condensation product decarboxylated **3** (%).
[c] Products **7a, b,** and **c** (%).
[d] Product **2** (%).
[e] Benzoic acid (%).
[f] Product **4** (%).
[g] Other products (%).

were reacted in the presence of basic zeolites.

By carrying out the Knoevenagel condensation with methylenic groups with different pK, it was found that the calcined hydrotalcite used here has basic sites with pK up to 16.5, most of them being in the range $10.7 \leq pK \leq 13.3$.

A method for titrating the basicity of the catalyst based on the condensation reactions using activated methylenic groups with different pK and benzoic acid is proposed.

Following this, it has been shown that the Michael and aldol condensations require strong basicities and, therefore, are much more sensitive to catalyst poisoning by acids than the Knoevenagel condensation.

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