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Condensation of glyceraldehyde acetonide and acetone over basic catalysts

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Abstract

A growing environmental concern is leading the chemical industry to develop environmentally benign products and processes. α,β-Unsaturated carbonyl compounds are important intermediates, however, their synthesis requires several steps and produces toxic wastes. The catalytic behavior of a Mg,Al-mixed oxide, derived from thermal decomposition of a hydrotalcite and an X zeolite exchanged with cesium and impregnated with cesium species was studied using the aldol condensation reaction between glyceraldehyde acetonide and acetone producing the corresponding α,β-unsaturated carbonyl compound. These catalysts were active for the studied reaction. The product distribution has shown that besides the principle product, other compounds obtained from different aldol reactions were observed. The rehydration of the Mg,Al-mixed oxide generated a catalyst that was selective to the condensation product of glyceraldehyde acetonide and acetone. The decrease of reaction temperature favored the formation of the main product over the Mg,Al-mixed oxide sample.

Keywords: Aldol condensation; Glyceraldehyde acetonide; Hydrotalcites; Mixed oxides; Basic zeolites; Sustainable chemistry

1. Introduction

2,3-O-isopropilydeneglyceraldehyde or glyceraldehyde acetonide is a compound largely used due to its characteristics, such as availability of enantiomers from natural resources and versatility related to the presence of the carbonyl group and the protected diol group [1,2]. α,β-Unsaturated carbonyl compounds obtained from glyceraldehyde acetonide are excellent Michael acceptors and one of the most used chirons in methodological studies and enantiomeric synthesis. The Wittig reaction using phosphorous ylids or phosphoranes has been used to synthesize these compounds. However, this kind of reaction presents several disadvantages, such as a large number of steps for the synthesis of phosphorous ylids and the production of triphenylphosphine as byproduct.

Considering the great applicability of these α,β-unsaturated carbonyl compounds and the disadvantages of their synthesis using the Wittig reaction, the study of new routes to produce them is very relevant in the field of organic intermediates production. One interesting synthetic route is the aldol condensation of glyceraldehyde acetonide with acetone (Fig. 1). It is an extremely chemoselective and convergent method to synthesize α,β-unsaturated carbonyl compounds and it is also an atom efficient route.

The aldol condensation is an important C–C bond forming reaction. When catalyzed by basic sites, the first step is the abstraction of an α-proton from an aldehyde or ketone. Then the carbanion formed attacks the carbonyl group of another aldehyde or ketone molecule to obtain a β-hydroxy aldehyde or ketone (aldol). Some aldols can be easily dehydrated in situ to α,β-unsaturated carbonyl compounds. This reaction is commonly used to manufacture solvents, plasticizers and intermediates for the manufacture of perfumes and pharmaceuticals. It can be carried out in heterogeneous medium over solid basic catalysts, such as zeolites, alkaline earth oxides and Mg,Al-mixed oxides or hydroxides derived from hydrotalcites [3–5].

The growing concern about the environment is leading the chemical industry to develop clean processes, which are

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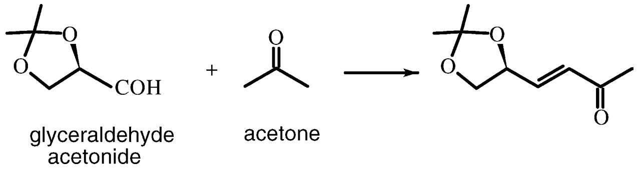

Fig. 1. Aldol condensation between glyceraldehyde acetonide and acetone.

based on the principles of the so-called Green Chemistry or Sustainable Chemistry [6]. The main goals of Green Chemistry are the efficient use of feedstocks, preferentially renewable resources, waste minimization and the substitution or elimination of toxic or dangerous reactants and solvents. In this context, solid catalysts have received increasing attention as substitutes for the highly pollutant liquid homogeneous catalysts in organic reactions in order to develop clean technologies. Moreover, the use of solid catalysts decreases corrosion risk and allows an easy separation and recovery of the catalyst.

The high surface area of zeolites and the possibility to tailor their acid–base properties for a desired process are important features of these materials that make them useful catalysts in several petrochemical and fine chemical processes. The zeolite basicity can be increased by decreasing the silica/alumina molar ratio (SAR), exchanging the compensation cations and impregnating basic compounds. Cesium-exchanged X zeolites impregnated with cesium basic compounds have been successfully used as basic catalysts in several reactions [3,7,8], including the synthesis of organic intermediates [9].

Similarly to that observed with zeolites, Mg,Al-mixed oxides derived from thermal treatment of hydrotalcites are among the solids that replaced homogeneous catalysts with considerable success. These materials present small particle size, large specific surface area and basic properties attributed to structural hydroxyl groups and O^{2-}–M^{n+} acid–base pairs [10,11]. The catalytic applications of Mg,Al-mixed oxides obtained from hydrotalcites include base-catalyzed reactions, such as aldol condensation of aldehydes and ketones and condensation of the carbonyl group with compounds presenting methylene-activated groups (for example, Knoevenagel and Claisen–Schmidt reactions) [4,12–14] and selective reduction of unsaturated ketones/aldehydes by hydrogen transfer from alcohols [15].

Different authors [16–21] have also shown that the rehydration of Mg,Al-mixed oxides in the absence of CO_2 enhances their activity for base-catalyzed reactions, such as aldol, Knoevenagel and Claisen–Schmidt condensations and Michael additions in liquid phase under mild conditions. The rehydration of the Mg,Al-mixed oxides gives rise to a meixnerite-like Mg,Al-hydroxide in which the original layered structure was restored and where the compensating anions are only hydroxide ions. These trends are explained by taking into account that the Lewis-type basic sites of the mixed oxides are converted into hydroxyl anions (Brönsted-type basic sites) upon rehydration and that this type of reactions are preferentially catalyzed by OH anions in liquid phase, as assumed in the classical organic mechanism [18].

In this work, the aldol condensation of glyceraldehyde acetonide and acetone catalyzed by a Mg,Al-mixed oxide, a sample obtained from the rehydration of the former one or a basic zeolite, was evaluated as an environmental friendly alternative route to the production of α,β-unsaturated carbonyl compounds, which have significant interest in organic synthesis. The influence of reaction temperature on the catalytic performance of the mixed oxides was also studied.

2. Experimental

2.1. Reagents

(*R*)-glyceraldehyde acetonide was prepared according to Mann et al. [22]: 1,2,5,6-di-O-isopropylidene-D-(+)-mannitol in THF solution reacted with an aqueous/THF solution of $NaIO_4$ under vigorous stirring during 1 h. Acetone, diacetone alcohol and all reagents used in catalysts preparation were technical grade.

2.2. Catalyst preparation

The hydrotalcite used as catalyst precursor, named HT, was prepared by coprecipitation, as previously described [4]. While stirring vigorously, an aqueous solution (solution A) containing $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ (1.5 M in (Al + Mg) with an Al/(Al + Mg) atomic ratio of 0.20) was slowly dropped into a highly basic carbonate solution (solution B), prepared by dissolving appropriate amounts of Na_2CO_3 and NaOH in distilled water so as to give a carbonate concentration of 1.0 M and a final pH of 10. The gel was aged at 333 K for 18 h. The solid obtained was then filtered and washed with distilled water (363 K) until pH 7.

The catalysts derived from the hydrotalcite sample were obtained using two different methods. In the first method, the hydrotalcite sample was calcined under air from room temperature up to 723 K at a 1 K min^{-1} heating rate and held at this temperature for 10 h, producing the Mg,Al-mixed oxide named MO. In the second method, sample MO was rehydrated under an air flow (100 mL min^{-1}) saturated with water at 298 K during 16 h at room temperature. This sample was identified as MO (h).

The zeolite sample used in this work was prepared from a sodium faujasite X (SAR = 2.3). This zeolite was exchanged twice with a cesium chloride solution at 353 K for 1 h, using a molar ratio of cesium in solution to total cations in the zeolite equal to 0.76 in each step. After each exchange step, the catalyst was filtered, washed with hot water and dried at 393 K. Next, the catalyst was impregnated with a cesium acetate solution according to the following procedure. A suspension containing the exchanged zeolite and a 2 M (cesium in solution to total cations in the zeolite equal to 6) solution of cesium acetate was prepared using the ratio of 1 g of zeolite/30 mL of solution and was agitated for 5 h at room temperature. After impregnation, the suspension was filtered without any washing process and dried at 373 K.

In order to decompose the impregnated cesium acetate into the active species, the sample was calcined at a rate of 5 K min^{-1} under a dry air flow, the temperature being held at 523 K for 30 min and at 673 K for 5 h. The sample was identified as CsX/CS.

2.3. Catalyst characterization

The chemical composition of the samples was determined by atomic absorption spectrometry (AAS) using a Perkin-Elmer AAS 1100B spectrometer. Thermal decomposition of the hydrotalcite sample was evaluated by thermogravimetric and thermodifferential analyses (TGA/DTA) carried out in a Rigaku Thermobalance TAS 100 under flow of air at 10 K min^{-1} up to 1273 K.

X-ray powder diffractograms were recorded in a Rigaku Miniflex X-ray diffractometer equipped with a graphite monochromator using Cu Kα radiation, 35 kV and 30 mA, in order to identify the crystalline phases present in the samples.

The crystalline framework of the zeolite samples was also checked by means of infrared spectroscopy. The spectra were recorded in a Perkin-Elmer 2000 Fourier transform infrared spectrophotometer at a resolution of 4 cm^{-1}. The wafers were prepared using 300 mg of KBr and 1 mg of zeolite.

Textural properties, such as specific surface area (BET), microporous volume (*t*-plot) and mesoporous volume (BJH) were determined by N_2 adsorption–desorption at 77 K in a Micromeritics ASAP 2000. Before the analysis, the samples were pretreated under vacuum overnight at 673 K (CsX/Cs and MO) or at 393 K (MO (h)).

The density and the strength distribution of the basic sites of the samples derived from hydrotalcite were determined by temperature-programmed desorption (TPD) of CO_2. The samples were produced in situ by the appropriate treatments described in Section 2.2. Pure CO_2 was adsorbed at room temperature and the sample was flushed with He to eliminate physically adsorbed molecules. TPD analyses were run under He at a heating rate of 20 K min^{-1} up to 723 K. The amount of CO_2 chemisorbed and its desorption profile were measured on a Micromeritics 2900 TPR/TPD analyzer with a quadrupole mass spectrometer detector (Balzers QMS-200).

2.4. Reaction procedure

The condensation reaction of glyceraldehyde acetonide and acetone was carried out in liquid phase without solvent in a stainless steel batch reactor magnetically stirred and heated by a thermostatic bath. The reaction system was maintained under nitrogen atmosphere and autogenous pressure. Immediately before the runs, sample MO was obtained by calcination of the parent hydrotalcite ex situ under the conditions described in Section 2.2 and rapidly transferred to the reactor containing the mixture of acetone and glyceraldehyde acetonide. Sample MO (h) was used without any additional pretreatment. The experimental conditions used were the following: reaction temperature = 298, 323 and 343 K; reaction time = 4 h; acetone/glyceraldehyde acetonide molar ratio = 30; 5 wt% of catalyst (referred to the total amount of reactants).

The reaction products were analyzed by means of a Chrompack 9000 gas chromatograph with a 50 m CP-Sil 5CB capillary column and a flame ionization detector. The identification of the products distribution was checked by means of a Hewllet Packard GC-HP 6890 gas chromatograph coupled to a Hewllet Packard HP 5973 mass detector.

3. Results and discussion

3.1. Physico-chemical properties of the catalysts

The X-ray diffractogram of the as-synthesized sample of hydrotalcite is shown in Fig. 2, along with those of its calcined form and of the mixed oxide after rehydration. It shows the characteristic pattern of hydrotalcite in carbonate form, whose main planes are indicated in the figure. Besides the hydrotalcite peaks, diffraction lines corresponding to a hydromagnesite (magnesium hydroxy-carbonate tetrahydrate, $4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$) phase were observed (marked with * in the figure). The presence of a small quantity of a phase different from hydroltacite was also observed by TGA/DTA and was associated to the high concentration of CO_3^{2-} and to the variation of pH from 14 to 10 during the preparation of the gel [23]. However, as shown by Pérez [24], the presence of small amounts of hydromagnesite does not influence the basic and catalytic properties of the Mg,Al-mixed oxide derived from hydrotalcite samples. For the calcined sample (MO), the XRD diffraction pattern indicates that the layered crystalline structure of hydrotalcite is destroyed and that a poorly crystallized periclase-type Mg(Al)O mixed oxide is formed. After rehydration, the original layered structure is partially restored, forming a meixnerite phase having OH^- as compensating anions ($MgAlOH_{14}{\cdot}xH_2O$) along with a small amount of remaining periclase. Similar trends were reported by different authors [17,19].

The TGA/DTA profiles of the as-synthesized material showed the two weight losses typical of hydrotalcite in carbonate form [25]. The first (15.6%), with a maximum rate at 473 K, is due to interlayer water and the second (20.5%), with a maximum rate at 673 K, corresponds to dehydroxylation and carbonate decomposition forming H_2O and CO_2. They also indicate a small loss of weight (<2%) near 850 K related to the hydromagnesite phase.

The Al/(Al + Mg) atomic ratio for the as-synthesized hydrotalcite, calculated by chemical analysis, was 0.20, very

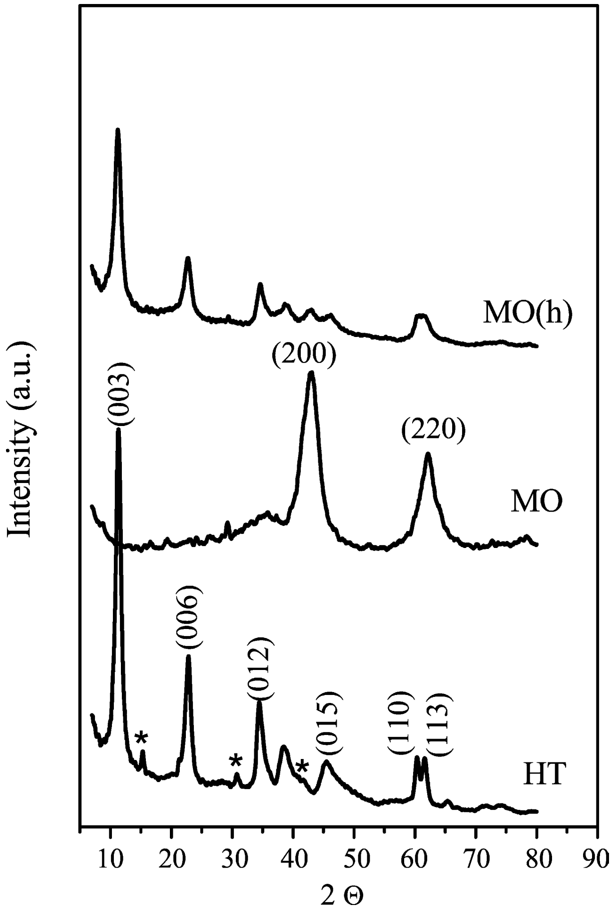

Fig. 2. X-ray diffraction patterns of the following samples: as-synthesized hydrotalcite, Mg,Al-mixed oxide and rehydrated mixed oxide.

similar to that of the synthesis gel, indicating a complete incorporation of both cations in the hydrotalcite structure. This result associated to that of TGA/DTA allowed the calculation of the chemical formula of the sample, which is presented in Table 1, along with that of the zeolite catalyst. It can be observed that the latter presented an exchange level for cesium of about 50% of the original sodium cations and 24 impregnated cesium atoms per unit cell as calculated from the TGA results.

The main textural characteristics of the catalysts derived from hydrotalcite and of the zeolite samples were determined by nitrogen adsorption and are shown in Table 2. Due to their size, the presence of cesium cations and impregnated cesium species causes a significant pore blocking of the zeolite. It is important to note that the low value of the microporous volume is not related to loss of crystallinity. The maintenance of the zeolite structure was verified by checking the infrared bands related to the vibrations of the zeolite crystalline framework in the region of 1300–300 cm^{-1}. Fig. 3 shows the infrared spectra of the three zeolite samples; no significant changes were observed in the range 1300–450 cm^{-1}, indicating that the ion exchange step and the impregnation of cesium species did not affect the crystallinity. The mixed oxide is fundamentally a mesoporous material, showing a very low value of microporous volume. As can be seen in Table 2, the rehydration of the Mg,Al-mixed oxide significantly reduced the porosity of the solid due to the reconstruction of the layered structure, which causes the agglomeration of the platelets closing mesopores [20,21].

Table 1
Chemical composition of the samples

Sample	Chemical formula
HT	$Mg_{6.4}Al_{1.6}(CO_3)_{0.8}(OH)_{16}\cdot 6.4H_2O$
CsX/CS	$Na_{46}Cs_{44}Al_{90}Si_{102}O_{384}\cdot 24CS$[a]

[a] Cesium atoms impregnated per unit cell.

Table 2
Textural characteristics of the samples

Sample	S[a] ($m^2\,g^{-1}$)	V_{meso}[b] ($cm^3\,g^{-1}$)	V_{micro}[c] ($cm^3\,g^{-1}$)
MO	271	0.47	0.04
MO (h)	45	0.15	–
NaX	701	0.02	0.32
CsX	464	0.01	0.22
CsX/CS	174	0.01	0.08

[a] Specific area (BET).
[b] BJH method.
[c] *t*-Plot method.

The profiles of CO_2 temperature-programmed desorption for the samples derived from hydrotalcites are presented in Fig. 4. Their comparison suggests that the rehydrated Mg,Al-mixed oxide sample contains a smaller proportion of strong sites. In order to quantify the basic site distribution, the profiles were deconvoluted into three desorption peaks with maxima in the ranges 400–420, 443–463 and 533–553 K. Deconvoluting into three peaks gave the best fit and agrees with previous results of Di Cosimo et al. [26]. Table 3 shows the relative contribution of each desorption peak and the basic site densities calculated from the amount of chemisorbed CO_2. The results presented in Table 3 indicate that for the Mg,Al-mixed oxide, the strong basic sites are predominant while for the rehydrated sample, half of the sites is of medium strength and that the latter sample has a lower basic site density. These results are in accordance with those of Rao et al. [18] which show that the rehydration process reduces the relative fraction of the strong basic sites, as also reported by Climent et al. [27] and decreases the total basic site density.

3.2. Catalytic results

The aldol condensation between glyceraldehyde acetonide and acetone was carried out over the prepared catalysts. The reaction products were identified using their retention time in gas chromatography and their mass spectra (taking into account the identification of the molecular ion and well-known mechanisms of fragmentation and considering the type of products expected for this aldol reaction).

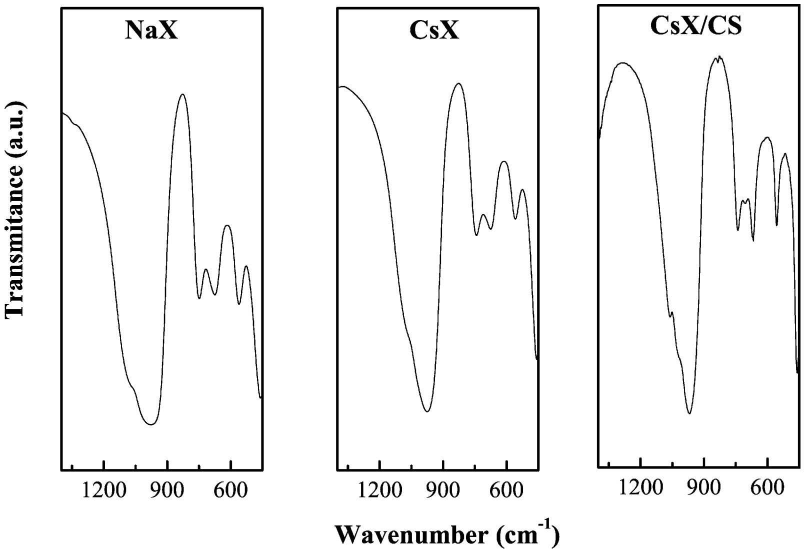

Fig. 3. Infrared spectra of the zeolite samples.

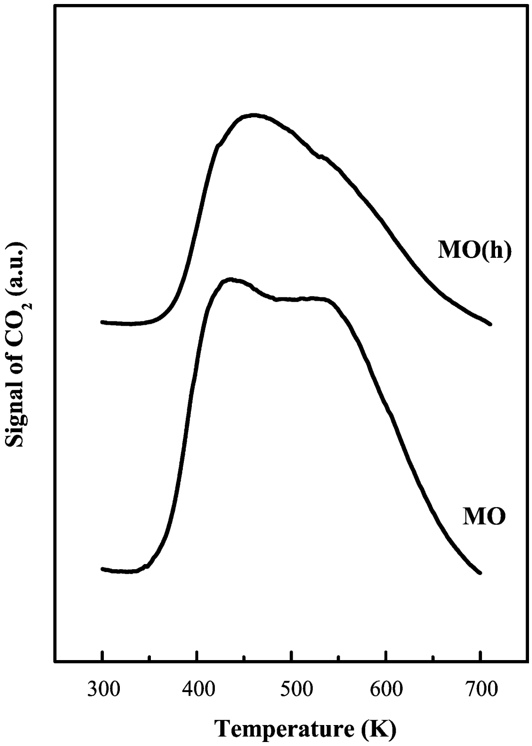

Fig. 4. Profiles of temperature-programmed desorption of CO_2: Mg,Al-mixed oxide, MO and rehydrated Mg,Al-mixed oxide, MO (h).

Under the experimental conditions studied, the following products were observed: product (**1**) formed from the aldol condensation between glyceraldehyde acetonide and acetone followed by the dehydration of the aldol condensation product (**3**) and product (**2**) obtained either from the aldol condensation between glyceraldehyde acetonide and diacetone alcohol, the latter being produced by the aldol self-condensation of acetone or by the aldol condensation between acetone and product (**3**) (Fig. 5). No reactions involving the α-proton of glyceraldehyde acetonide were observed, probably due to the steric hindrance of the isopropelidenic portion.

The results of glyceraldehyde acetonide conversion and selectivity to products (**1**), (**2**) and diacetone alcohol are given in Table 4. All samples were active for the reaction of interest and selective to product (**1**), while product (**2**) was obtained using samples CsX/CS and MO. However, especially with the catalysts derived from hydrotalcite, a significant amount of diacetone alcohol was observed.

The first step in the aldol condensation of glyceraldehyde acetonide and acetone is the abstraction of an α-proton from acetone on a basic site forming a carbanion that could attack the carbonyl group of the glyceraldehyde acetonide or of another acetone molecule (Fig. 5). As the carbonyl group of an aldehyde is more reactive than the same group of a ketone, the acetone carbanion reacts preferentially with

Table 3
Results of temperature-programmed desorption of CO_2 for the Mg,Al-mixed oxide samples

Sample	Basic site density (μmol of CO_2 g^{-1})	Desorption peaks (area %)		
		Low temperature peak (400–420 K)	Medium temperature peak (443–463 K)	High temperature peak (533–553 K)
MO	437	13	20	67
MO (h)	271	20	50	30

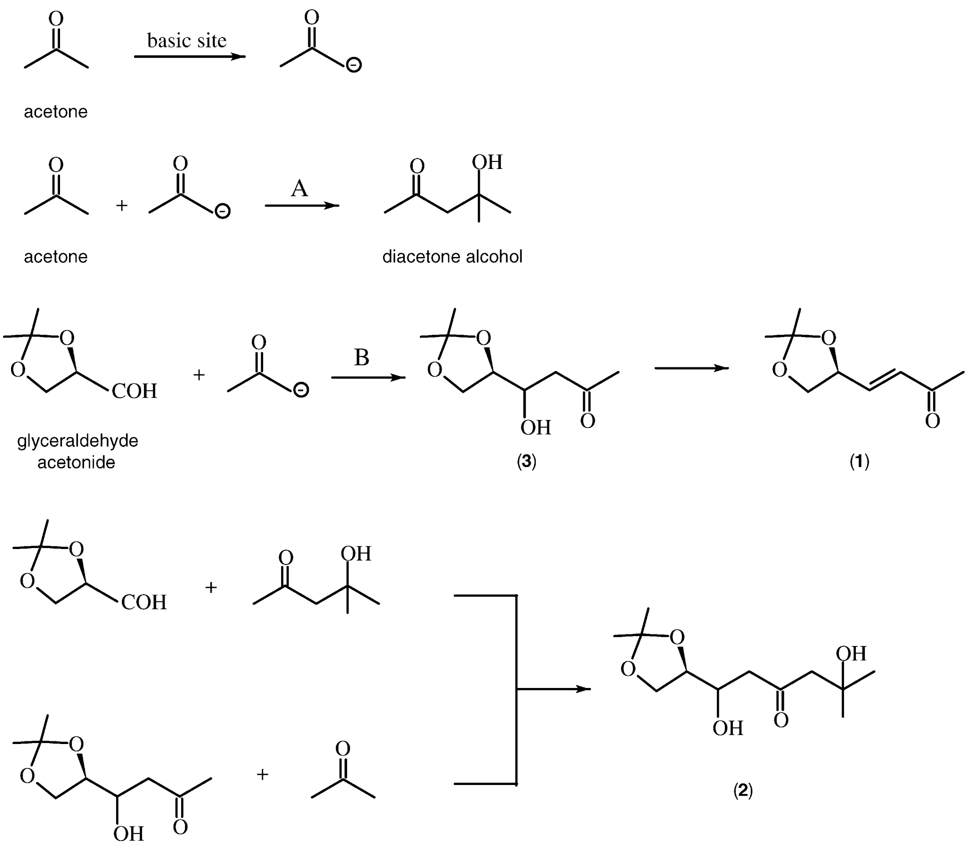

Fig. 5. Main reactions observed for the condensation between glyceraldehyde acetonide and acetone.

glyceraldehyde acetonide requiring a site that presents a low basic strength.

A comparison of the catalytic behavior of samples CsX/CS and MO at 323 K shows that both catalysts present a conversion of glyceraldehyde acetonide of about 50% and produce products (**1**), (**2**) and diacetone alcohol, but the Mg,Al-mixed oxide shows a higher selectivity to diacetone alcohol. However, similar selectivities to products (**1**) and (**2**), when only these products were considered, are observed. These catalysts have Lewis basic sites of different strength. As the basic sites of the Mg,Al-mixed oxide are stronger than those of the zeolite [27], the former catalyst is capable of catalyzing routes A and B presented in Fig. 5 leading to a higher selectivity to diacetone alcohol. A similar behavior was reported by Climent et al. [27] when comparing the performance of zeolites and mixed oxides for other condensation reactions. However, the higher basicity of the Mg,Al-mixed oxides derived from hydrotalcites did not affect the condensation reactions in which the glyceraldehyde acetonide was involved because the strength of the basic site required for these reactions is low due to the high reactivity of the aldehyde carbonyl group.

Table 4
Catalytic results for the condensation of glyceraldehyde acetonide and acetone

Sample	Conversion (%)	Selectivity (%)		
		(**1**)	(**2**)	DAA[a]
MO	47.9	46.1 (92.3)[b]	3.9 (7.7)	50.0
MO (h)	53.0	65.8 (100)	–	34.2
CsX/CS	50.7	83.6 (93.9)	5.5 (6.1)	10.9

$T = 323$ K; reaction time = 4 h; acetone/glyceraldehyde acetonide molar ratio = 30; 5 wt% of catalyst.

[a] Diacetone alcohol.

[b] The selectivity values presented in parenthesis represent the selectivity only to products (**1**) and (**2**).

As can be seen in Table 4, the rehydration process of the Mg,Al-mixed oxide slightly improves its catalytic activity and inhibits the formation of product (**2**). Thus, only product (**1**) and diacetone alcohol were observed as reaction products. The lower selectivity to diacetone alcohol over the rehydrated mixed oxide sample, MO (h), indicates a decrease in the aldol condensation of acetone. According to the literature [17–21], the rehydration of a mixed oxide increases the catalyst activity to condensation reactions in liquid phase. When this process is done in the absence of CO_2, it restores the original layered structure where the compensating anions in the interlayer are now hydroxyl groups. It also converts the Lewis basic sites into Brönsted ones, although up to now, little is known about the nature and the number of active Brönsted basic sites generated.

The results of temperature-programmed desorption of CO_2 shown in this work indicate that most of the basic sites of the mixed oxide sample are strong ones while those of the rehydrated mixed oxide are mainly of intermediate strength.

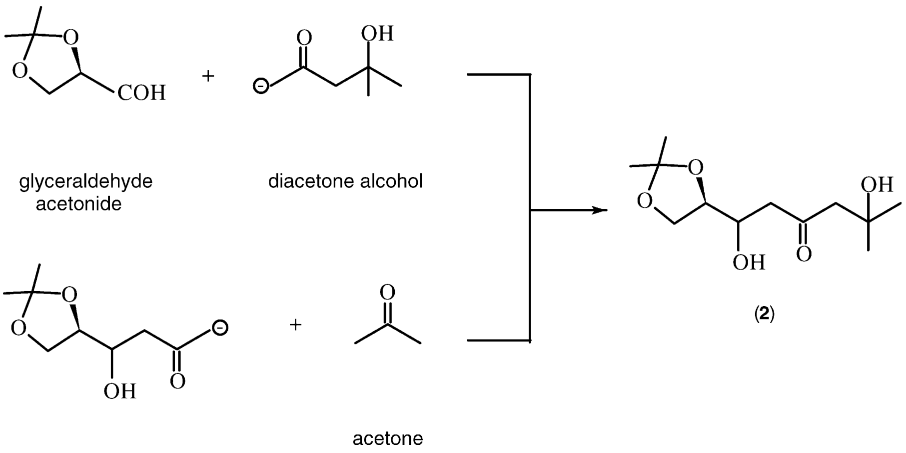

Fig. 6. Different possible pathways to product (**2**).

Similar observations were presented by Climent et al. [27] who furthermore state that the mixed oxide presents Lewis-type sites (O^{2-}–M^{n+} pairs) and the rehydrated sample presents Brönsted-type basic sites (hydroxyl ions). The presence of intermediate Brönsted-type basic sites favored preferentially the condensation between glyceraldehyde acetonide and acetone increasing the selectivity to product (**1**) and inhibited the self-condensation of acetone that requires stronger basic sites. Probably, the presence of Brönsted-type basic sites inhibits the formation of product (**2**) due to a weak interaction between this type of site and compounds containing hydroxyl groups. Product (**2**) could be formed by two different pathways, but both of them require the formation of a carbanion upon compounds containing hydroxyl groups (Fig. 6).

The influence of the reaction temperature was evaluated using sample MO and the results are shown in Table 5. As expected, the conversion of glyceraldehyde acetonide increased as the reaction temperature increases. A higher selectivity to product (**2**) is also observed, showing that the routes to obtain this product (Fig. 6) are significantly influenced by reaction temperature. Particularly, at 298 K, product (**2**) was not observed.

In this work, the diastereoselectivity of the process is not under investigation. New experiments to develop mildest reactional conditions and improve the regioselectivity are in progress.

Table 5
Catalytic results for the condensation of glyceraldehyde acetonide and acetone over a Mg,Al-mixed oxide

Sample	T (K)	Conversion (%)	Selectivity (%)		
			(**1**)	(**2**)	DAA[a]
MO	298	12.8	56.4 (100)	–	43.6
MO	323	47.9	46.1 (92.3)[b]	3.9 (7.7)	50.0
MO	343	73.0	53.1 (83.6)	10.4 (16.4)	36.5

Reaction time = 4 h; acetone/glyceraldehyde acetonide molar ratio = 30; 5 wt% of catalyst.

[a] Diacetone alcohol.

[b] The selectivity values presented in parenthesis represent the selectivity only to products (**1**) and (**2**).

4. Conclusions

A Mg,Al-mixed oxide derived from hydrotalcite and a cesium-exchanged/cesium-impregnated zeolite were active for the aldol condensation between glyceraldehyde acetonide and acetone. For both catalysts, other products were observed, besides the principle product, such as diacetone alcohol, obtained from acetone self-condensation and product (**2**) obtained either from the aldol condensation between glyceraldehyde acetonide and diacetone alcohol or from the aldol condensation between acetone and product (**3**).

At 343 K, the activities of the Mg,Al-mixed oxide and the zeolite were similar, but a lower selectivity to diacetone alcohol was observed over the zeolite sample due to its lower basic strength. The rehydration of the Mg,Al-mixed oxide produced intermediate basic sites generating a catalyst that was selective to the condensation product of glyceraldehyde acetonide and acetone, although diacetone alcohol was still produced. Probably, a weak interaction between compounds with hydroxyl groups and the Brönsted-type basic sites of the rehydrated Mg,Al-mixed oxide inhibits the formation of product (**2**).

For the Mg,Al-mixed oxide, the decrease of the reaction temperature decreased the formation of product (**2**) increasing the relative selectivity to the main product.

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