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INFLUENCE OF THERMAL TREATMENTS ON THE BASIC AND CATALYTIC PROPERTIES OF Mg,Al-MIXED OXIDES DERIVED FROM HYDROTALCITES

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Abstract - This work studied the influence of calcination conditions on basic properties and catalytic performance of Mg,Al-mixed oxides derived from a hydrotalcite sample (Al/(Al+Mg)=0.20). Various heating rates, calcination atmospheres and lengths of calcination at 723K were evaluated. TPD of CO_2 and retroaldolization of diacetone alcohol (DAA) were used to determine the basic properties of the mixed oxides. The basic site density determined by TPD of CO_2 showed a better correlation with catalytic activity for acetone/citral aldol condensation than the relative basicity obtained from retroaldolization of DAA. Calcination atmosphere was the parameter that influenced most the basic and the catalytic properties of the Mg,Al-mixed oxides, with calcination under dry air being the best choice.

Keywords: hydrotalcites, Mg,Al-mixed oxides, thermal treatment, aldol condensation, citral, acetone.

INTRODUCTION

Hydrotalcites are layered double magnesium-aluminum hydroxides with the general formula: $[Mg_{8-x}Al_x(OH)_{16}(CO_3^{2-})_{x/2}].nH_2O$, whose structure consists of brucite-like layers where partial substitution of Al^{3+} for Mg^{2+} cations results in an excess of positive charge which is compensated by carbonate anions located with water molecules in the interlayer space (Tichit et al., 1995). They can be synthesized using different methods (Cavani et al., 1991), the most common of which is the coprecipitation at constant pH of diluted solutions containing Mg^{2+} and Al^{3+} cations with solutions containing carbonate and hydroxide ions (Reichle et al., 1986; Corma et al., 1994; Tichit et al., 1995). The precipitate is quite amorphous, but after ageing by hydrothermal or thermal treatments its crystallinity is improved (Del Arco et al., 1993). The Al/(Al+Mg) ratio in hydrotalcites varies between 0.20 and 0.33 (Cavani et al., 1991). Many systems have been synthesized to be used as anion exchangers or adsorbents (Tichit et al., 1995). In recent years, hydrotalcites have attracted attention as precursors of mixed oxides with basic properties.

Thermal treatment of hydrotalcites induces dehydration, dehydroxilation and loss of compensation anions, forming the Mg,Al-mixed oxides with basic properties and a poor crystallized MgO-type structure (McKenzie et al., 1992; Rey et al., 1992; Del Arco et al., 1993; Tichit et al., 1995). These oxides have a small particle size, large specific surface area and basic properties attributed to structural hydroxyl groups, O^{-2} - M^{+n} acid-base

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*To whom correspondence should be addressed pairs and O^{2-} anions (Di Cosimo et al., 1998), so they are potentially useful as adsorbents and as heterogeneous base catalysts and catalytic supports. As shown by different authors, the surface basic properties and consequently catalytic performance depend on chemical composition, with the optimum Mg/Al ratio depending on the basic site density and strength required to activate the reactant of the reaction under study (Sharper et al., 1989; Corma et al., 1994; Velu and Swamy, 1994; Climent et al., 1995; Di Cosimo et al., 1998).

When calcination of hydrotalcite is carried out at temperatures lower than 823K, the mixture of oxides shows the so-called “memory effect” and reconstructs the original hydrotalcite structure simply by exposure to carbonate anions in aqueous solution or to humid air during several days (Reichle et al., 1986). On the other hand, if the material is calcined above 1100K, a mixture of MgO and $MgAlO_4$ (spinel) will be irreversibility obtained (Rey et al., 1992).

The applications in catalysis of Mg,Al-mixed oxides obtained from hydrotalcites include base-catalyzed reactions such as aldol condensation of aldehydes and ketones, condensation of the carbonyl group with compounds having activated methylene groups (for example, Knoevenagel and Claisen-Schmidt reactions), alkene isomerization, alkylation of di-ketones and phenols and alkene epoxidation activated by hydrogen peroxide (Sharper et al., 1989; Corma et al., 1992; 1993; 1994; Velu and Swamy, 1994; Cativela et al., 1995; Climent et al., 1995; Tichit et al., 1995; Guida et al., 1997; Rao et al., 1998). Some of those reactions are associated with the production of fine chemicals and intermediates such as citronil (used in the perfume and soap industries), chalcones and flavonoids (for the pharmaceutical industry) and alkylated phenols (organic intermediates).

Catalysts obtained by calcination of Mg,Al-hydrotalcites are potential substitutes for the most common bases used in industry, such as hydroxides or carbonates of alkaline or alkaline-earth metals, salts of ammonium or amines, among others. The ease of separation from the reaction mixture and the possibility of reutilization are other advantages of these catalysts, which are also environmentally friendly (Tichit et al., 1995).

The base-catalyzed aldol condensation of citral ($C_{10}H_{16}O$) and acetone (C_3H_6O) producing pseudoionones (6,10-dimethyl-3,5,9-undeca-trien-2-one) is an example of a process involving products obtained from essentials oils (citral) of great commercial interest since pseudoionones are intermediates in the synthesis of ionones, which are extensively used in the perfume and soap industries and as precursor in the synthesis of vitamin A (β-ionone) (Noda Pérez et al., 1986). Figure 1 shows the scheme for production of ionones from citral and acetone.

Pseudoionones are commercially produced from the aldol condensation of citral and acetone catalyzed by aqueous or ethanolic solutions of bases. However, these liquid catalysts have potential problems related to undesirable side reactions (self-condensation of citral and secondary reactions of pseudoionones), catalyst separation and disposal (the catalyst cannot be reused and causes serious damage to the environment) and purification steps, which are laborious and costly (Noda Pérez, 2001). These homogeneous processes also require a large excess of acetone, typically 10-20 moles per mole of citral, for a satisfactory yield, and a large and costly plant is needed for commercial production.

These problems could be overcome with the use of basic solid catalysts. Of these, the Mg,Al-mixed oxides/hydroxides derived from hydrotalcites show potential, as shown by different authors (Noda Pérez et al., 1998; Roelofs et al., 2000; Bastiani, 2001; Noda Pérez, 2001; Roelofs et al., 2001). In the present work, we report on the effect of different calcination conditions of a hydrotalcite sample on the basic properties of the Mg,Al-mixed oxides so obtained and on their catalytic performance in the aldol condensation of citral and acetone. The use of temperature-programmed desorption of CO_2 (TPD of CO_2) and of the reaction of diacetone alcohol retroaldolization as tools to characterize the basic properties of those catalysts are also discussed.

EXPERIMENTAL

Reagents

The citral used, containing 98 wt-% of the isomers geranial and neral, was purchased from MERCK-Schuchardt. Acetone (99.5 wt-%, technical grade) was dried and distilled to reduce the water content to less than 0.07 wt-%. Diacetone alcohol (98 wt-%, mesityl oxide content less than 2 wt-%) and all reagents used in hydrotalcite synthesis were also of technical grade.

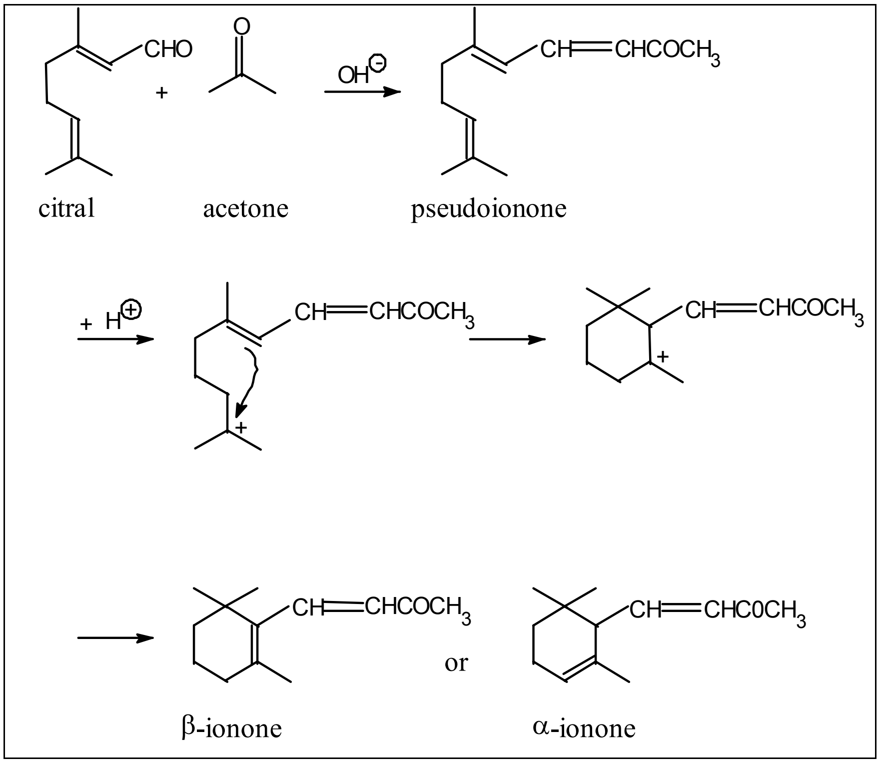

Figure 1: Production of α and β-ionones from citral.

Catalyst Preparation

The hydrotalcite used as catalyst precursor was prepared by coprecipitation, as previously described by Noda Pérez (2001). While stirring vigorously, an aqueous solution (solution A) containing $Mg(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ (1.5M 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 appropriated 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 333K for 18 h. The solid obtained was then filtered and washed with distilled water (363 K) until reaching pH 7.

The catalytically active form of hydrotalcite was obtained upon thermal decomposition at 723K. Aiming at optimizing this thermal treatment, different calcination conditions were evaluated and related to the basic and catalytic properties of the mixed oxides obtained. Table 1 shows the different calcination parameters studied, namely carrier gas/vacuum, heating rate and time span at 723K and the sample codes.

Table 1: Different thermal treatments evaluated for obtention of Mg,Al-mixed oxides from hydrotalcite

Catalyst	Calcination atmosphere (100mL/min)	Heating rate (K/min)*	Time (h)**
HT0110	Dry air	1	10
HT1010	Dry air	10	10
HT1005	Dry air	10	5
HT1015	Dry air	10	15
HT1010N	N_2	10	10
HT1002V	Vaccum	10	2
HT1010W	Dry air saturated with decarbonated water at 293K	10	10

*Final temperature of 723K
**Calcination time at 723K

Catalyst Characterization

The chemical composition of the synthesized sample was determined by atomic absorption spectrometry (AAS) using a Perkin-Elmer AAS 1100B spectrometer. X-ray powder diffraction patterns were recorded in a Rigaku X-Ray generator equipped with a graphite monochromator using CuKα radiation, 40 KV and 40 mA. Thermal decomposition of this sample was evaluated by TGA and DTA carried out in a Rigaku Thermobalance TAS 100 under a stream of air at 10 K/min up to 1273 K.

The textural characteristics (BET specific surface area, microporous and mesoporous volumes) of some of the Mg,Al-mixed oxides obtained by calcining the parent hydrotalcite under the conditions shown in Table 1 were determined by N_2 adsorption-desorption at 77 K in a Micromeritics ASAP 2000. Before the analysis, the mixed oxides were thermally treated *in situ* at 473K under vacuum overnight.

Characterization of Basic Properties

a) Temperature Programmed Desorption of CO_2

The catalytically active forms of hydrotalcite (Mg,Al-mixed oxides) were analyzed by temperature programmed desorption (TPD) of CO_2, aiming at determining the strength and the basic sites distribution. The amount of CO_2 chemisorbed and its desorption profile for each sample were measured on a Micromeritics 2900 TPR/TPD analyzer with a quadrupole mass spectrometer detector. Prior to analysis, the original hydrotalcite (± 500 mg) was thermally treated under the conditions shown in Table 1. Next, it was cooled down to room temperature for CO_2 adsorption (60mL/min, 60 min) and then flushed with He (60 mL/min, 30 min) to eliminate physically adsorbed CO_2. TPD analyses were run under He (30 mL/min) at a heating rate of 20 K/min up to 723K.

b) Retroaldolization of Diacetone Alcohol

This reaction was studied in a fixed-bed microreactor at 1atm, 313K and a WHSV (gram of acetone per hour per gram of catalyst) of $19.3h^{-1}$. The reactant was fed into the reactor by bubbling nitrogen (170mL/min) through a saturator containing acetone held at 303K. Before the reaction, the original hydrotalcite was calcined *in situ* under the different conditions presented in Table 1. Then the system was cooled down to 313K and the reaction began. The exit stream was regularly analyzed by on-line gas chromatography (50m CP-Sil 5CB column on a Chrompack 9000 gas chromatograph).

Catalytic Tests - Aldol Condensation of Citral and Acetone

The reaction was carried out in liquid phase using a 50mL stainless steel batch reactor, magnetically stirred and heated with an oil bath. The active form of the catalyst was obtained by calcination *ex-situ* under the conditions described in Table 1. After activation, the catalyst was rapidly transferred to the reactor containing the mixture of acetone and citral. The system was then purged with N_2 and heated up to the reaction temperature. The catalytic tests were carried out at 398K, under autogenous pressure, using an acetone/citral molar ratio of 1 with the amount of catalyst being 1 wt-% of the reaction mixture. Reaction time was 4 h. The products were analyzed by gas chromatography using a 50 m Carbowax 20 M capillary column in a Chrompack 9001 chromatograph (FID detector). The samples were dissolved in n-hexane (technical grade) before analysis. The reaction products were identified by gas chromatography-mass spectrometry in a Shimatzu GC/MS - QP 2000 A.

RESULTS AND DISCUSSION

Hydrotalcite Characterization

The Al/(Al+Mg) molar ratio for the synthesized hydrotalcite, calculated by chemical analysis, was 0.20, similar to that of the synthesis gel, indicating a complete incorporation of both cations in hydrotalcite structure. The X-ray diffraction pattern of this solid, shown in Figure 2, has diffractions peaks for the carbonate form of hydrotalcite and low-intensity peaks ascribed to hydromagnesite. Similar results were reported by Noda Pérez (2001) and were associated with both the high concentration of CO_3^{2-} and the pH, which decreased from 14 to 10 during preparation of the gel (Rey, 1992). The presence of this small quantity of hydromagnesite did not influence the basic and the catalytic properties of the mixed oxide derived from hydrotalcite (Noda Pérez et al., 2001).

The TGA/DTA profiles (Figure 3) showed two losses of weight, typical of hydrotalcite in carbonate form (Reichle et al., 1986; Reichle, 1986; Belloto et al., 1996). The first (15.6 wt-%) is due to interlayer water, and the second (20.5 wt-%), corresponds to dehydroxylation and carbonate decomposition forming H_2O and CO_2. These results and those of the chemical analysis were used to calculate the chemical formula of the hydrotalcite used as precursor: $Mg_{6,4}Al_{1,6}(CO_3)_{0,8}(OH)_{16}\cdot 5,86H_2O$.

Textural Characterization of the Mg,Al-Mixed Oxides

The inspection of N_2 adsorption/desorption isotherms for some of the mixed oxides samples indicated that they presented IUPAC type IV isotherms, confirming that the thermal decomposition of the hydrotalcite produced mesoporous Mg,Al-mixed oxides with negligible micropore volumes. As can be seen in Table 2, the differences in the textural characteristics of the samples were small enough so that no significant influence of calcination conditions (time span and atmosphere) could be detected.

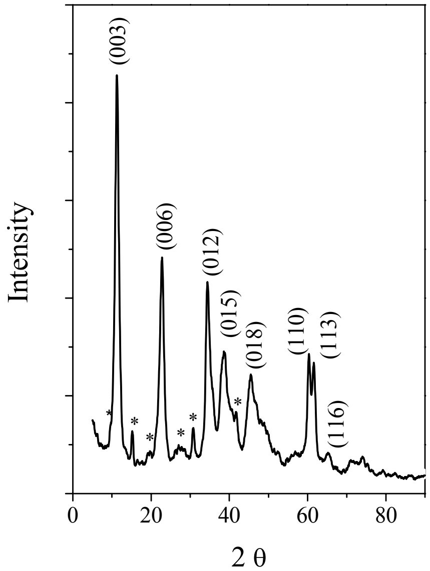

Figure 2: X-ray diffractogram for the synthesized hydrotalcite.

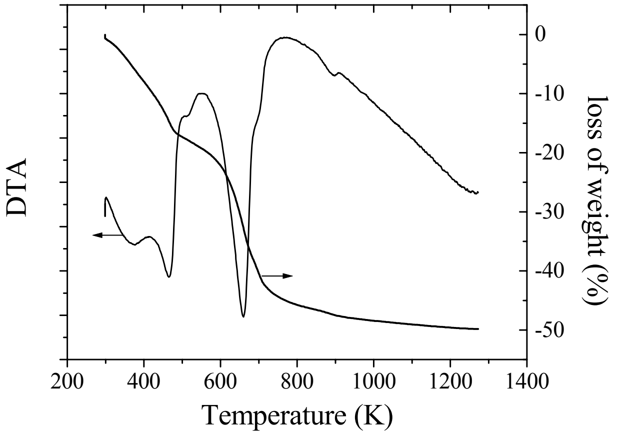

Figure 3: TG/DTA profiles for the synthesized hydrotalcite.

Table 2: Textural characteristics of Mg,Al-mixed oxides

Sample	HT1010	HT1005	HT1010N	HT1010W
S_{BET} (m^2/g)	215	207	222	192
V_{meso}[a] (cm^3/g)	0,47	0,48	0,45	0,51

[a] BJH adsorption branch (17-600 Å).

Basic Properties of the Mg,Al-Mixed Oxides

a) Temperature Programmed Desorption of CO_2

The thermograms corresponding to CO_2 temperature-programmed desorption are shown in Figure 4. No significant differences are observed in the desorption profiles for the Mg,Al-mixed oxides derived from hydrotalcite calcined under different conditions, except for the high temperature region in the case of the sample calcined in air saturated with decarbonated water at 293K. This suggests that the latter sample contains a smaller proportion of strong sites.

The profiles were deconvoluted in three desorption peaks, reaching maximum desorption rate in the ranges 400-420K, 443-463K and 533-553K. Table 3 shows the relative contribution of each individual desorption peak calculated by the integration of its profile. It can be observed that the high temperature peak is predominant on all samples, except HT1010W. This result indicates that the use of air saturated with decarbonated water as atmosphere of calcination probably has a negative effect on the strong basic sites, which are thus formed in a smaller proportion.

Di Cosimo et al (1998) studying mixed oxides derived from HTLCs also observed that the TPO profiles could be deconvoluted in three peaks with different basic strength. The authors associated their results to those obtained from the infrared spectra of adsorbed CO_2 and related the L.T.peak (low-strength basic sites) to surface hydroxyl groups and the M.T. (medium stength basic sites) and H.T. (high strengh basic sites) peaks to surface basic oxygen atoms.

Table 3 also contains the basic site densities calculated from the amount of chemisorbed CO_2. The results indicate that this parameter was not influenced by either the heating rate or the lenght of calcination at 723K, since the amounts of chemisorbed CO_2 are quite similar for samples HT0110, HT1005, HT1010 and HT1015. On the other hand, the calcination atmosphere has a strong influence on this property, since the samples calcined in N_2 or humid air chemisorbed less CO_2 than the samples thermally treated in dry air under the same conditions. Thus, samples HT1010N and HT1010W had the lowest basic site densities, an effect that was more important for sample HT1010W.

b) Retroaldolization of Diacetone Alcohol

The use of retroaldolization of diacetone alcohol (DAA) in gas phase at 313K as a model reaction for characterization of relative basicity of solid catalysts was first proposed by Veloso and Monteiro (2000). The reaction is easy to perform and its results are readily interpreted, since acetone is the only product formed via basic catalysis, as shown in Figure 5. A good correlation for the basicity of CsX and CsY zeolites impregnated with cesium species, MgO and hydrotalcite was reported by the authors (Veloso and Monteiro, 2000).

In the present work, diacetone alcohol retroaldolization was used aiming at comparing the relative basicities of the mixed oxides derived from the hydrotalcite sample by different thermal treatments. The results, expressed as a function of diacetone alcohol conversion, are presented in Figure 6.

The atmosphere of calcination and the heating rate show no significant influence on activity for diacetone alcohol retroaldolization, as can be observed when the results of samples HT0110, HT1010, HT1010N and HT1010W are compared, although the results of TPD of CO_2 showed differences in basic site density between the samples calcined in different atmospheres. The results associated with samples calcined at 723K for 10 and 15h (HT1010 and HT1015, respectively) were also similar. However, a significant reduction in diacetone alcohol conversion was observed for the sample calcined only during 5h (HT1005). Again, a difference between the basic properties determined by TPD of CO_2 and by the model reaction was observed, since samples HT1005, HT1010 and HT1015 had similar basic site densities measured by TPD of CO_2.

The differences observed between the relative basicities determined by TPD of CO_2 and the model reaction can be attributed to both the different interactions between the “probe molecule” (CO_2 or DAA) and the basic sites and the different sizes of the two molecules. While TPD is associated with chemisorption of the acid molecule (CO_2) on the basic sites, retroaldolization of DAA involves chemisorption of this molecule and abstraction of a proton from its hydroxyl group. These differences agree with previous observations of the lack of a single technique for characterization of basic sites on solids (Barthomeuf, 1995).

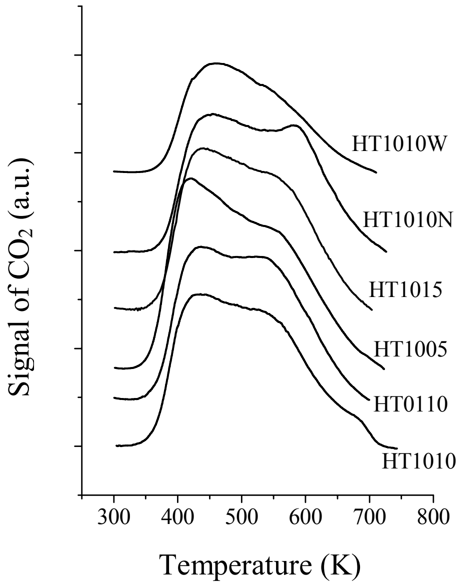

Figure 4: TPD of CO_2 thermograms associated with the Mg,Al-mixed oxides produced from hydrotalcite using different calcination conditions.

Table 3: Basic properties of the Mg,Al-mixed oxides: TPD of CO_2 results.

Catalyst	**Basic site densities (μmol de CO_2/g)**	**Desorption peaks (area %)**		
		L.T.P.[a] 400-420K	**M.T.P.[b] 443-463K**	**H.T.P.[c] 533-553K**
HT0110	437	13	20	67
HT1010	451	13	17	70
HT1005	425	15	24	61
HT1015	403	15	25	60
HT1010N	335	13	33	54
HT1010W	271	20	50	30

[a] L. T. P. = low temperature peak;
[b] M.T.P. = medium temperature peak;
[c] H.T.P. = high temperature peak

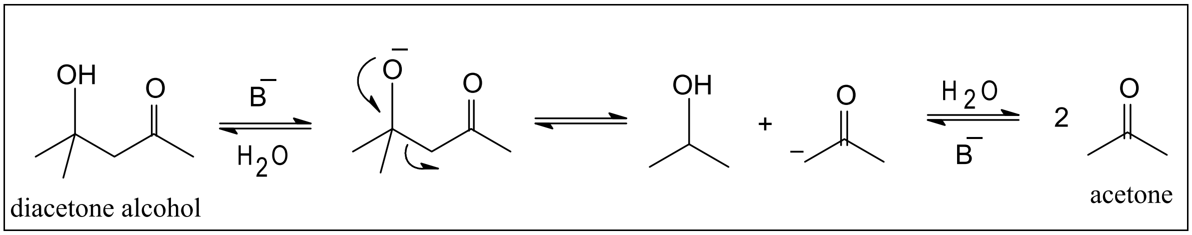

Figure 5: Diacetone alcohol retroaldolization scheme.

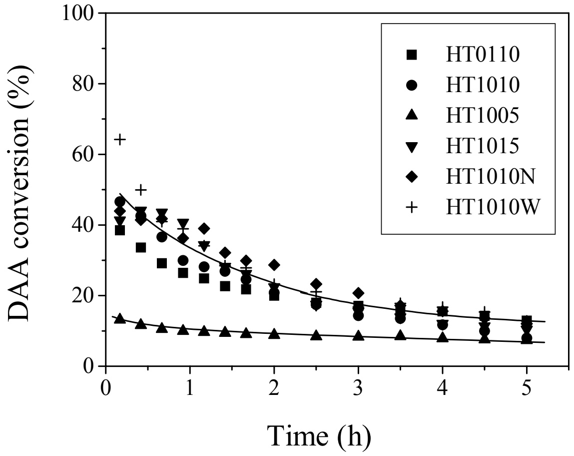

Figure 6: Diacetone alcohol conversion for the different catalysts evaluated (P = 1atm, T = 313K, WHSV = 19.3 g $_{acetone}$/h.g$_{catalyst}$)

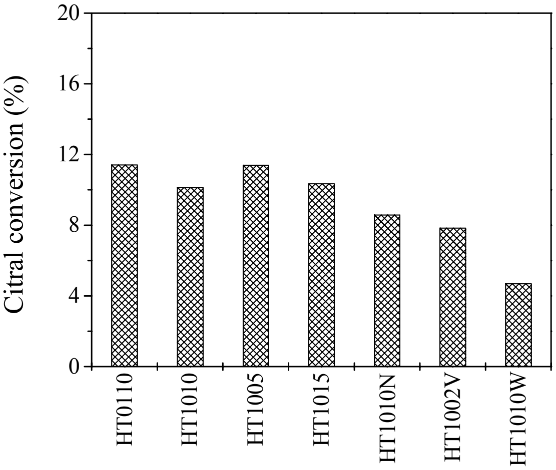

Figure 7: Citral conversion (%) obtained with the Mg,Al-mixed oxides produced from hydrotalcite under different calcination conditions (T = 398K, autogenous pressure, acetone/citral molar ratio = 1, catalyst content = 1 wt-% of the reaction mixture, reaction time = 4 h).

Catalytic Tests - Aldol Condensation of Citral and Acetone

The main products formed from the aldol condensation of acetone and citral catalyzed by Mg,Al-mixed oxides were the two isomers of pseudoionone (PSI_A and PSI_B). Other compounds observed were those from the condensation of two citral molecules (PCS) or of pseudoionone isomers and one acetone molecule (Noda Pérez, 2001).

The main results for the reaction catalyzed by the different Mg,Al-mixed oxides obtained by calcination of a hydrotalcite sample are presented in Figures 7 and 8. They show that the calcination atmosphere is the parameter that most influenced the catalytic performance of the mixed oxides. As can be observed in Figure 7, the highest citral conversions were found for the samples calcined in dry air, with heating rate and time of calcination having no significant influence on catalytic performance within the range explored.

These results indicate that the basic site density obtained by TPD of CO_2 correlates better with the catalytic activity for citral/acetone condensation than does the relative basicity established by retroaldolization of DAA or the textural characteristics of the samples. This can be associated with the fact that although both reactions are base-catalyzed, they require different basic site strengths, since the first step of DAA retroaldolization involves abstraction of a proton from a hydroxyl group while aldol condensation is initiated by abstraction of an alpha proton from a methyl group, with the latter requiring greater basic strength.

Figure 8 shows that the differences among the Mg,Al-mixed oxides obtained under different calcination conditions were not sufficient to influence significantly reaction selectivities (PSI and PCS). This result is in accordance with those of Noda Perez (2001), who showed that for the reaction catalyzed by Mg,Al-mixed oxides with different Al contents and studied under similar conditions (T=398K, t=4h and acetone/citral molar ratio=1) the differences in the basic, textural and morphological properties of the catalysts did not affect selectivity for the reaction products.

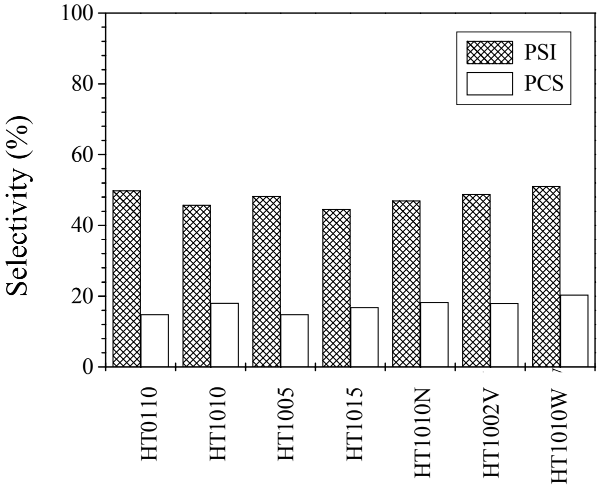

Figure 8: PSI and PCS selectivities (%) obtained with the Mg,Al-mixed oxides produced from hydrotalcite under different calcination conditions (T = 398K, autogenous pressure, acetone/citral molar ratio = 1, catalyst content = 1 wt-% of the reaction mixture, reaction time = 4 h).

CONCLUSIONS

The evaluation of the influence of calcination conditions on the basic properties and catalytic performance of Mg,Al-mixed oxides obtained from hydrotalcite indicated that heating rate and time of calcination at 723K play a minor role. The calcination atmosphere, on the other hand, was shown to have a marked influence on catalytic activity. Calcination in dry air was the best choice for a good performance of the catalyst in citral/acetone aldol condensation. The activity of the catalysts for retroaldolization of DAA did not correlated with their activity for citral/acetone condensation reaction, indicationg that these two reactions required sites with different strengths.

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