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Activation of Mg–Al Hydrotalcite Catalysts for Aldol Condensation Reactions

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The condensation of benzaldehyde and acetone to aldol has been investigated in the liquid phase at 273 K on hydrotalcites transformed into basic solids by activation following different procedures. No activity was observed on the pure hydrotalcite (carbonated) or on the solid just decarbonated at 723 K. The activity went through a maximum after calcination at 723 K, followed by rehydration by water vapor at room temperature. The calorimetric determination of the adsorption of carbon dioxide demonstrated a lower basicity on the rehydrated surface, compared to the mixed oxide. Traces of chlorine retained in the synthesis were detrimental for catalytic properties. An aldol yield higher than 85 mol% was obtained after optimum activation. The higher activity of the rehydrated sample suggests that aldolisation in the heterogeneous phase is specifically catalyzed by hydroxide ions. © 1998 Academic Press

INTRODUCTION

Layered double hydroxides (LDHs) or hydrotalcite like compounds (HTLCs) have recently received much attention (1) in view of their potential usefulness as adsorbents, anion exchangers, and most importantly, as basic catalysts (2–4). These compounds are represented by the formula $[M^{2+}_{(1-x)}M^{3+}_{x}(OH)_2]^{x+}(A^{m-}_{x/m})\cdot nH_2O$, where the divalent ion may be Mg^{2+}, Ca^{2+}, Zn^{2+}, Ni^{2+}, and the trivalent ion Al^{3+}, Fe^{3+} or Cr^{3+}. The compensating anions may be OH^-, Cl^-, NO_3^-, CO_3^{2-}, SO_4^{2-}, and x can take values between 0.25 and 0.33 (5, 6). It is an alternating layered structure with positively charged brucite like layers $(M^{2+}M^{3+}(OH)^-)$, where M^{2+} cations are substituted by M^{3+} cations and interlayers contain the charge balancing anions and water molecules.

Numerous studies on the physico chemical properties and thermal stability of various LDHs have been reported (7–9). Upon thermal decomposition, a highly active homogeneous mixed oxide is obtained from these materials at about 723 K which is potentially a basic catalyst for a variety of organic transformations such as aldol condensations (10), olefin isomerization (2), nucleophilic halide exchange (11), alkylation of diketones (12), epoxidation of activated olefins with hydrogen peroxide (13), or Claisen–Schmidt condensation (14).

The aldol condensation has numerous applications in the synthesis of fine chemicals, classically catalyzed by bases (15). For a better protection of the environment it is desirable to find solid bases which could substitute liquid catalysts and would also show all the advantages of heterogeneous catalysis, i.e. ease of separation of the products, decreased corrosion of the reactor, and possible regeneration of the catalyst. At the laboratory scale many catalysts have been proposed including alumina (16, 17), zeolites (18), sepiolite (19), and hydrotalcites (14, 20). It has to be remarked that if high conversions can be reached with these solids, the yields are generally modest. In a former work (20), the condensation of acetone with benzaldehyde was investigated at 383 K; the observation of a good Hammett correlation showed that the aldolisation was, indeed, base-catalysed on hydrotalcites and that traces of chlorine left on the solid strongly inhibited the catalytic properties by blockage of the stronger basic sites.

In all these former studies, aldolisations were performed at relatively high temperatures of about 673 K for the addition of formaldehyde to acetone (10), 573 K for the condensation of acetone (21), and 383 K for the condensation of benzaldehyde with ketones (12, 20). Thermodynamic data are scarce for this type of reaction, but it appears that the aldolisation of acetone is an exothermic reaction, so that the yield decreases with increasing temperature. The work at 383 K, for instance, gives low yields in aldol, and the main product is then benzalacetone, obtained by dehydration of the aldol. The reaction was, therefore, performed here in an ice bath, i.e. 273 K. Moreover, the results recently reported on the activation of hydrotalcites (22) were taken into account.

The present work was aimed at discovering the activation conditions which selectively provide aldol, instead of the dehydrated products which were the major products obtained in earlier work (14, 21). Therefore, Mg–Al hydrotalcites were synthesised by different methods, and

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basic properties were modified by suitable activation conditions.

EXPERIMENTAL

(1) *Synthesis of Hydrotalcites*

Two methods of synthesis were used, based on previous work.

(1) *Procedure* A (20). Two aqueous solutions (0.5 L), the first one containing 0.3 mol of $MgCl_2 \cdot 6H_2O$ and 0.1 mol of $AlCl_3 \cdot 6H_2O$ (Aldrich-Chemie) for a composition Mg/Al = 3 and the second one containing 0.8 mol of NaOH and 0.02 mol of Na_2CO_3, were slowly mixed at 343 K under vigourous stirring, maintaining the pH between 8 and 10. The mixture was heated at this temperature for 15 h under stirring. The precipitate was washed several times until the solution was free of chloride ions ($AgNO_3$ test). The products were dried at 313 K. This sample is referred as HYD1.

Exchange of Cl^- anions. 2 g of HYD1 was suspended in a 1.5×10^{-3} M solution of sodium carbonate (100 mL) and stirred at 343 K for 2 h. After filtration the solids were washed and dried at 353 K. This sample is further referred to as HYD1A.

(2) *Procedure* B (23). An aqueous solution (0.187 L) containing $Mg(NO_3)_2 \cdot 6H_2O$ (0.1875 mol) and $Al(NO_3)_3 \cdot 9H_2O$ (0.093 mol) for a ratio Mg/Al = 2, was added slowly to a second solution (0.187 L) containing NaOH (0.4375 mol) and Na_2CO_3 (0.1125 mol) in a 0.500 L round-bottom flask under vigourous stirring. The addition took nearly 3 h. Then the contents were heated to 338 K for 16 h. The precipitate formed was filtered and washed with hot distilled water until the pH of the filtrate was 7. The precipitate was dried in the oven at 353 K for 15 h. Hydrotalcites with different Mg/Al ratios of 2, 2.5, and 3 were synthesised and labelled as HYD10, HYD11, and HYD12, respectively, These samples were not further exchanged by carbonates.

$Mg(OH)_2$ (Aldrich-Chemie) was used for comparison studies after activation similar to the hydrotalcites.

(2) *Activation of the Catalysts*

Catalysts were first activated by calcining to 723 K in a flow of air. The temperature was raised at the rate of 10 K/min to reach 723 K and maintained for 8 h. The solid was then cooled in dry nitrogen and rehydrated at room temperature under a flow of nitrogen gas saturated with water vapour. The flow of wet nitrogen of 6 L/h was maintained for a specified period, depending on the amount of catalyst to be rehydrated.

(3) *Characterisations*

X-ray powdered diffraction patterns were recorded with a PW1050/81 Philips automated goniometer (Bragg–Brentano parafocussing geometry). The CuKα radiation (0.154184 nm) was selected by a graphite monochromator placed before the scintillation detector. Coupled thermogravimetry (TG) and differential thermal analysis (DTA) were carried out in a Setaram apparatus at a heating rate of 5°C/min, in air, using 40 mg each of the sample. The surface area of the samples were measured by employing the BET adsorption method. Before doing the experiments the samples were first treated in air at 723 K for 8 h and then under vacuum at 623 K for about 4 h. Elemental analysis of Mg^{2+} and Al^{3+} of these samples was carried out by inductively coupled plasma analysis by dissolving the compounds in a minimum amount of dilute hydrochloric acid.

The adsorption of CO_2 was followed both by calorimetry and measurements of uptake using the experimental apparatus described elsewhere (24). After outgassing the sample at 673 K, CO_2 was introduced in small increments. The heat of adsorption of CO_2 can be taken as a measure of the basic strength of the adsorption sites, and the distribution in strengths of basic sites was obtained using the differential heat of adsorption as a function of coverage. Measurements were also performed on a sample rehydrated at room temperature by contact with water vapour and then outgassed in vacuum at 373 K.

(4) *Reaction Procedures*

Several experiments were conducted for understanding the reaction conditions of the aldolic condensation reaction of benzaldehyde and acetone. Benzaldehyde (Aldrich) was kept over NaA molecular sieves to trap possible traces of benzoic acid, and acetone (Normapur AR) was used as received. The acetone to benzaldehyde ratio was 32. Typically, acetone, 11.85 ml (160 mmol) and benzaldehyde 0.51 ml (5 mmol) were taken into a three-necked 50 ml round-bottom flask and cooled to 273 K with ice. After 15 min of cooling, the freshly activated catalyst (0.19 g) was introduced and the progress of the reaction followed through HPLC (Shimadzu) using KROMASIL C8 (5 μ, 100 A) column and using a UV detector at 195 nm wavelength in a mixture of acetonitrile and water in the ratio of 55 : 45 with a flow rate of 0.4 mL/min.

Since the product 4-hydroxy-4-phenyl-butan-2-one (Aldol) is not available commercially to standardise in HPLC, it was isolated, after conducting the reaction, by column chromatography using hexane and ethylacetate as the eluent. The purity and authenticity of the product was ascertained by characterising through ^1H NMR and ^{13}C NMR (Bruker AC100 instrument):

^1H NMR (100 MHz) (δ ppm, $CDCl_3$)—2.16(s, CH_3); 2.84(m, CH_2); 5.11(dd, CH); 7.31(m, C_6H_5).

^{13}C NMR (25.178 MHz) (δ ppm, $CDCl_3$)—30.72(CH_3); 52.33(CH_2); 70.15(CH); 125.93, 127.89, 128.77, and 143.28 (Ar); 209.08(C=O).

TABLE 1

Chemical Composition and Crystallographic *c* and *a* Parameters of Different Mg/Al Hydrotalcite Samples

Sample	Composition	*c* (Å)	*a* (Å)
HYD1A[a]	Mg0.749Al0.251$(OH)_2(CO_3)$0.125, 0.73 H_2O	23.421	3.062
HYD10	Mg0.687Al0.313$(OH)_2(CO_3)$0.16, 0.85 H_2O	22.851	3.046
HYD11	Mg0.714Al0.286$(OH)_2(CO_3)$0.143, 0.70 H_2O	23.094	3.055
HYD12	Mg0.744Al0.256$(OH)_2(CO_3)$0.128, 0.73 H_2O	23.325	3.063

[a] Trace amounts of Cl^- present in these samples.

RESULTS AND DISCUSSION

(1) *Synthesis and Characterization of Hydrotalcites*

The structural formulas given in Table 1 were established from the chemical analysis of the solids and thermogravimetric analysis presented in Table 2. The *c* and *a* parameters were calculated from the (003) and (110) XRD peaks. The surface areas and porosities are presented in Table 3.

The X-ray diffraction patterns of hydrotalcites are reported in Fig. 1; these catalysts show crystalline hydrotalcite patterns, indicating the formation of the compounds. After calcination at 723 K, their structure is that of mixed oxide of the MgO type, and after hydration the original hydrotalcite structure was reformed (Fig. 1). The values of the unit cell parameters, assuming rhombohedral symmetry, with the *c* parameter corresponding to three times the thickness of the expanded brucite like layer, are included in Table 1. The *a* and *c* parameters (Table 1) decreased with increasing aluminum content and which can be explained by the substitution of larger Mg^{2+} ions by smaller Al^{3+} ions (25).

TG and DTA analysis. The TGA-DTA data are reported in Table 2. These catalysts showed two stages of weight loss characteristic of HTLCs (23). Each weight loss is accompanied by an endothermal transformation. The first weight loss is noticed between 490 and 515 K for all the samples and can be attributed to the loss of interlayer water molecules. The second weight loss is noticed between 680 and 688 K and is attributed to the removal of condensed water molecules and carbon dioxide from the carbonate anion present in the brucite layer. The second peak usually appears broad because of the simultaneous loss of water and carbon dioxide. From the literature (23), it is noticed that initially CO_2 is lost, followed by the loss of water molecules in the brucite sheet.

TABLE 2

Thermal Analysis Results

Sample	First weight loss%	Temperature (K)	Second weight loss%	Temperature (K)
HYD1A	16.57	490	26.67	682
HYD10	18.18	521	26.23	688
HYD11	15.80	515	26.91	686
HYD12	16.46	495	26.31	683

TABLE 3

Surface Properties of the Catalysts

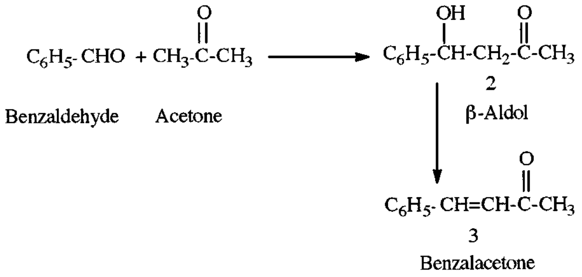
Sample	Surface area (m^2/g)	Pore diameter range (nm)	Pore volume (cm^3/gm)
HYD1A	185	16–34	0.595
HYD10	281	20–26	0.844
HYD11	275	15–35	0.674
HYD12	288	15–35	0.664

Basicity from CO_2 adsorption. The results are reported in Figs. 2 and 3, in which two hydrotalcite samples just calcined, or calcined then rehydrated are compared. It appears that the calcined sample is more basic than the rehydrated one, both in strength and number of sites. The higher amount of CO_2 adsorbed and the higher heat of interaction show that surface oxygens have a higher basicity than OH groups. Therefore water inhibits the stronger basic sites.

From these physico-chemical characterizations the solids used here appear as pure hydrotalcites, which reproduce the solids described in the literature.

(2) *Catalytic Activity*

(1) *Kinetics of the reaction.* The aldolisation of benzaldehyde with acetone has been carried out to study the catalytic activity. The main product obtained is 4-hydroxy, 4-phenyl butan-2-one (β-aldol), with small amounts of benzalacetone formed by dehydration:



Neither benzyl alcohol or benzoic acid were observed in the reaction products using MgAl hydrotalcites as catalyst precursor, therefore the Cannizzaro reaction is not catalyzed under these conditions. A representative reaction profile is presented in Fig. 4, obtained using the experimental conditions described in the experimental section and HYD11 as catalyst. It is noticable that the conversion reaches 90% in 2 h and 94% in 3 h, with a selectivity to aldol of 86%. The formation of benzalacetone is considerably less (6%). The remaining 8% are due to small amounts of unknown

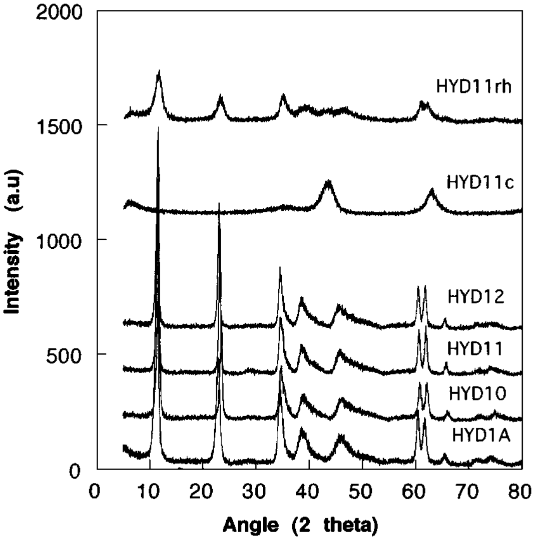


FIG. 1. Powder X-ray diffraction patterns of hydrotalcites.

products observed in HPLC analysis, which are difficult to identify. They may include products of a aldolisation of benzalacetone, for instance, dibenzalacetone.

The initial rate as a function of the weight of the catalyst (HYD12) proved to be proportional to the weight of the catalyst, indicating that external mass transfer does not limit the kinetics. Typical values of the rate of reaction are 10^{-5} mol $s^{-1} \cdot g^{-1}$, with an average particle size <0.1 mm, and a substrate concentration of 0.5 mmol mL^{-1}. The criterion of Weisz (26),

$$\frac{dN}{dt}\frac{1}{C_0}\frac{R^2}{D_{\text{eff}}} = \Phi$$

in which C_0 is the concentration of reactant (mol/mL), R (cm) is the radius of the catalyst particles, dN/dt (mol/s/g) is the rate and D_{eff} (cm^2/s) the diffusion coefficient, permits us to estimate the importance of internal diffusion. The low value of the Weisz modulus $\Phi = 0.2$ ensures that the kinetics is not greatly perturbed by diffusion.

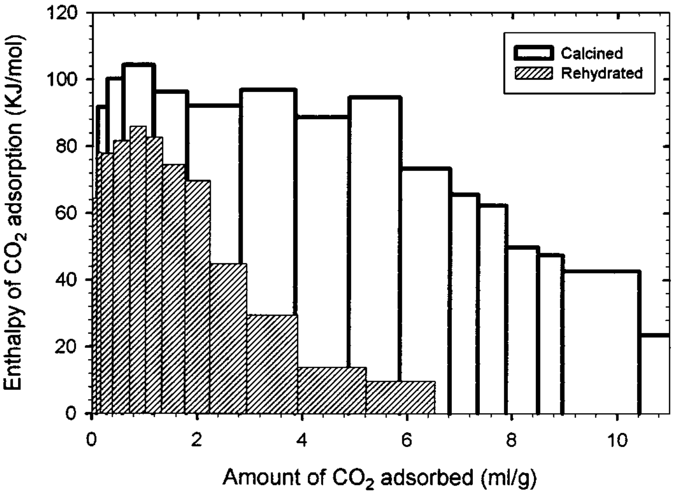


FIG. 2. Enthalpies of adsorption of carbon dioxide on hydrotalcite (Mg/Al = 2.7) calcined at 723 K and on the same sample calcined at 723 K and rehydrated at room temperature.

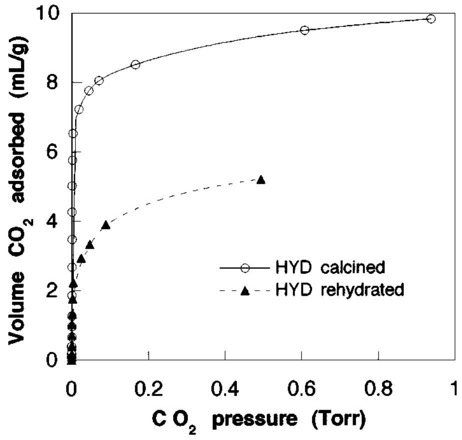


FIG. 3. Isotherms of adsorption of CO_2 on hydrotalcite (Mg/Al = 2.7) calcined at 723 K and on the same sample calcined at 723 K and rehydrated at room temperature.

From the experimental curves of concentration versus time, the initial rates of reaction can be determined. These rates, determined for different concentrations of benzaldehyde are plotted against the concentration in Fig. 5. Benzaldehyde behaves as a inhibitor of the reaction. A competitive Langmuir Hinshelwood mechanism in which benzaldehyde and acetone compete for the same basic sites has been proposed for barium oxide by Aguilera *et al.* (27) and for hydrotalcites at higher temperature by Guida *et al.* (28). This competitive mechanism was interpreted by Aguilera *et al.* (27) by a reaction occurring between the carbanion produced from the reaction of acetone with a basic site and the adsorbed aldehyde.

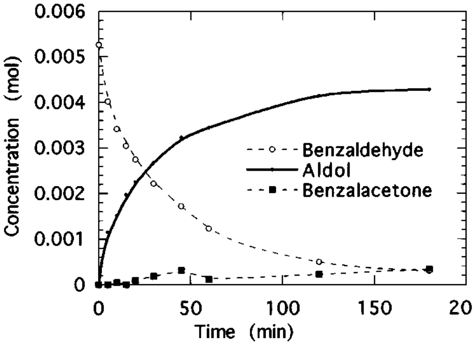


FIG. 4. Reaction profile of reaction between acetone and benzaldehyde with catalyst HYD11 (weight of nonactivated catalyst, 0.195 g), using standard reaction conditions: acetone 160 mmol, benzaldehyde 5.2 mmol, and temperature 273 K.

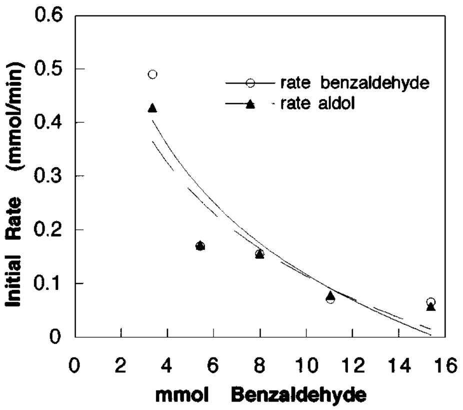


FIG. 5. Initial reaction rate at 273 K as a function of the number of millimoles of benzaldehyde added to acetone acting also as solvent. The catalyst is HYD12, and the weight of sample is 0.19 g before activation.

In the resulting rate equation,

$$r = k\lambda_A\lambda_B C_A C_B/(1 + \lambda_A C_A + \lambda_B C_B)^2, \quad [1]$$

a negative order for benzaldehyde is reached if we assume a stronger adsorption for benzaldehyde than for acetone. From the kinetic study of this reaction on the same catalyst sample at 383 K, in ethanol as solvent, a set of values $\lambda_A = 1.2$ and $\lambda_B = 41–53$ was obtained (28). Therefore benzaldehyde is, indeed, much more strongly adsorbed than acetone at 383 K. Since adsorption is exothermic, the adsorption coefficient decreases with temperature; therefore the adsorption coefficient of benzaldehyde is expected to be much higher at 273 K, as the ratio λ_B/λ_A. This accounts for the inhibiting effect of benzaldehyde at 273 K and for the reduction of the general rate equation to

$$r = k\lambda_A C_A/\lambda_B C_B. \quad [2]$$

Plotting the rate against the $1/C_B$ ($C_B =$ concentration of benzaldehyde) gives a straight line, reported in Fig. 6 in the range of concentrations used.

A linear correlation between the rate of condensation of benzaldehyde on acetone catalyzed by hydrotalcites and the σ Hammett parameter characterizing substituent effects was reported earlier (20). The slope of the line was comparable to that obtained for NaOH in the liquid phase and, therefore, showed that aldolisation followed a basic mechanism. Since aldolisation on hydrotalcite is catalyzed by basic sites it can be used to characterize basicity.

(3) *Effect of the Temperature of Calcination*

In order to determine the influence of the calcination temperature, HYD11 was activated at different temperatures between 673 and 873 K and rehydrated as described in the experimental section before measuring the activity. The initial reaction rates determined after calcination at different temperatures are reported in Table 4. The Experimental conditions are the same as described in the experimental section.

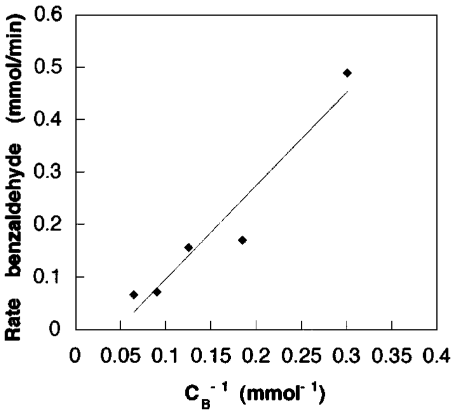


FIG. 6. Linearized form of the rate equation, in which C_B stands for the concentration of benzaldehyde.

The maximum activity is observed at 748 K and a low level of activity is observed below 723 K and above 798 K. Constantino and Pinnavaia (29) recently reported that a catalyst, active for the conversion of 2-methyl-3-butyne-2-ol, was obtained below its decomposition temperature (<523 K). The application of similar conditions of activation of the catalysts (including the catalyst synthesised following the same method used by these authors) for our reaction, gave no conversion at all. Hence, we conclude that the reaction investigated here requires a much higher basic strength than that of 2-methyl-3-butyne-2-ol, and thus, a much higher decomposition of the carbonates.

(4) *Influence of Rehydration after Calcination*

The initial rate of the reaction as a function of hydration time is presented in Table 5. The experimental conditions are the same as described in the experimental section and HYD11 is used for these studies. It is clear that rehydration of the sample is essential in order to get an active catalyst for this kind of reaction. There is very little activity when

TABLE 4

Initial Rate as a Function of the Calcination Temperature, Using the Standard Reaction Conditions: Acetone 160 mmol, Benzaldehyde 5.2 mmol, Temperature 273 K, Weight of Sample 0.19 g

Calcination temperature (K)	Initial rate (mmol/min/g)
673	0.40
698	0.42
723	1.28
748	1.36
773	1.34
798	1.19
873	0.45

TABLE 5

Initial Reaction Rate as a Function of the Length of the Hydration Time

Time of hydration (h)	Initial rate of the reaction (mmol/min/g)
0 (only calcination)	0.03
1	0.13
3	1.1
5	1.1
7	1.3
9	1.2

Note. Reaction conditions as in Table 4.

TABLE 6

Activity of Different Catalysts in Terms of Initial Rate of the Reaction

Catalyst	Mg/Al	Initial rate of the reaction (mmol/min/g catalyst)
$Mg(OH)_2$	—	0.01
HYD1	3	0.49
HYD10	2.04	1.25
HYD11	2.5	1.28
HYD12	2.91	1.14
HYD1A	2.98	2.36

Note. Reaction conditions similar to Table 4.

a sample which has only been calcined is used and the rate of the reaction is increased progressively until 7 h of hydration; after that a small drop in activity is observed. The main effect of rehydration is to increase the reaction rate, since the selectivity remains relatively high on the calcined sample. Since calorimetry shows a lower basicity of the surface after rehydration, both in strength and number of sites, it has to be concluded that aldolisation is rather specific of OH^- and works worse on oxygens even if the basic strength is higher.

(5) *Effect of the Reaction Temperature*

When the reaction was conducted at ambient temperature (298 K) using the catalyst HYD11 the initial rate of the reaction was increased 3.3 times compared to the rate of the reaction conducted at 273 K, but the selectivity towards aldol decreased from 86 to 71% and that towards benzalacetone increased from 6.3 to 22%. The activation energy for dehydration is apparently higher than that of aldolisation, and this result explains why little aldolisation has been observed previously at 373 K.

(6) *Comparison of the Activities of Different Hydrotalcites*

The benzaldehyde conversion as a function of time for different catalysts is shown in Fig. 7. and the initial rates of the reactions are presented in Table 6. The catalyst obtained from $Mg(OH)_2$ with the same activation procedure is found to be very poor. The order of reactivity of the catalysts for the Aldol reaction is

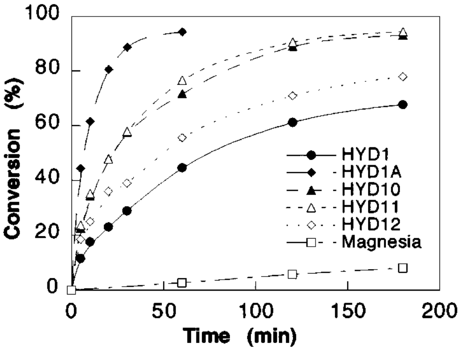


FIG. 7. Conversion as a function of time for different hydrotalcites.

$$Mg(OH)_2 \ll HYD1 < HYD12 < HYD11 = HYD10 < HYD1A.$$

The low activity of HYD1 can be attributed to the retention of traces of chlorine, as reported previously (20). The series of samples prepared from nitrates with Mg/Al ratios between 2.2 and 2.9 show only a small change of the activity with the Mg/Al ratio and a small decrease at the higher ratio, in agreement with the report of Climent *et al.* (14), for a similar reaction at higher temperatures. It is interesting to observe that the activity of the sample prepared from the chlorides and further exchanged by carbonates is higher by a factor of 2. The surface areas of the exchanged sample HYD1A is lower (185 m^2/g) than that of sample HYD12 prepared from the nitrates (288 m^2/g), and the difference can then hardly be due to a different particle size as proposed by Corma *et al.* (14) in other cases. Since trace amounts of Cl can induce great changes of activity, the different activities are tentatively attributed to these impurities in the nitrate precursors, which in that case are not eliminated by anionic exchange.

CONCLUSIONS

A good yield of aldol can indeed be obtained in heterogeneous catalysis using hydrotalcites, provided the solid is suitably activated and the reaction is performed at a low temperature. The rehydration step is essential for a good selectivity, as formerly reported for the aldolisation of acetone. When the basic sites are oxygens, a stronger basicity but a lower activity are observed. This result suggests that aldolisation is catalysed by OH^-, as assumed in the classical organic mechanism.

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