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Catalytic condensation of aromatic aldehydes with acetone on activated Mg–Al mixed oxides

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Abstract

The factors affecting the aldol condensation of some model aromatic aldehydes (benzaldehyde, the three isomers of F-benzaldehyde and 2-naphthaldeyde) with acetone have been investigated using heterogeneous catalysts obtained by the calcination of hydrotalcite-type (HT) precursors at 773 K for 8 h, followed by rehydration at room temperature for 7 h under a flow of N_2 saturated with water vapour. At 273 K the main product was the β-hydroxy-ketone, while at 318 K it mainly dehydrated to the corresponding *trans*-arylideneacetone, with small amounts (<10 wt%) of by-products as *cis*-arylideneacetone, 1,3-diarylideneacetone and 4-hydroxy-4-methyl-2-pentanone. High reaction times favoured the formation of *trans*-arylideneacetone. The best conversion values were observed for the three F-benzaldehydes and while using an HT catalyst with Mg/Al = 2.5 as atomic ratio. Finally, a significant improvement of the productivity per kg of catalysts has been achieved by repeatedly adding new amount of aromatic aldehyde to the reaction mixture when the conversion value was about 80% ca., thus developing a semi-continuous process.

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1. Introduction

Hydrotalcite-type (HT) anionic clays, have been proposed as catalysts or catalyst precursors for many reactions of industrial interest [1–5]. In particular, in the most recent years, many applications have been claimed for the selective synthesis of fine chemicals catalysed by bases or multifunctional catalysts, see for example [3–15]. These catalysts are unexpensive, relatively simple to prepare and may be used in these reactions either in laboratory or on industrial scale.

Recently, interesting data have been reported on the use of the Mg/Al mixed oxides [Mg–Al (O)] obtained by the calcination of HT precursors in the condensation reaction of benzaldehyde with acetone (Fig. 1) [16–18]. Generally, a high conversion of benzaldehyde was achieved, with the β-hydroxy-ketone (Fig. 1, compound 3) as main reaction product at low reaction temperature, catalysed by basic hydroxyls [17]. It is noteworthy that a very high increase of activity has been reported for the Mg–Al (O) catalysts obtained by the calcination of the HT precursor at 773 K followed by rehydration by water vapour at room temperature [18]. This result has been explained by de Jong and co-workers [19] that proposed a model in which only basic sites near the edges of the HT platelets are partaking in aldol condensation. Besides incorporating interlayer OH^- upon rehydration, the hexagonal morphology changed as a result of activation into a more irregular but still layered structure, with an enhanced activity of interlayer OH^- close to disordered edges.

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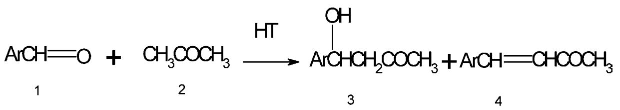

Ar = phenyl; 2-, 3-, or 4-fluorophenyl; 2-naphthyl.

Fig. 1. Aldol condensation of the investigated aromatic aldehydes with acetone.

Aim of this study was to deeply investigate the latter modified HT catalysts and the factors affecting the HT-catalysed condensation reactions of some model aromatic aldehydes (benzaldehyde, 2-naphthaldehyde, 2-, 3- and 4-fluoro-benzaldehydes, since fluorine derivatives have potential industrial applications) with acetone, that in order, to establish the limits of the industrial application of HT catalysts, in consideration of the relevance of the aldol condensation step in the synthesis of intermediates or fine chemicals.

2. Experimental

The HT precursors, with different Mg/Al atomic ratios (4.0, 2.5 and 2.2), were prepared by co-precipitation at pH 10.0 ± 0.1 and 323 K, by slowly adding the solution of the Mg and Al nitrates to a solution of Na_2CO_3/NaOH. The composition of the final HT precursors was controlled by chemical analysis [20]. After separation and drying at 383 K, the HT precursors were calcined at 723 K for 8 h and rehydrated at room temperature for 7 h under a flow of N_2 saturated with water vapour [18,19]. All the reagents (Aldrich) were at least of analytical grade. Not purified acetone was used, while the aromatic aldehydes were previously purified by extraction with a 2 N solution of NaOH and subsequently dehydrate by using anhydrous Na_2SO_4 to remove any trace of the corresponding acid.

The aldehyde (40 mmol) was dissolved in an excess of acetone (1600 mmol) and the solution heated to 318.0 ± 0.5 K 2.0 g of activated HT catalyst were added and the mixture stirred at a rate of 450 ppm under N_2. At different times, 3.0 mL samples were taken and filtered from the catalyst, then 2.0 mL were diluted with acetone to 10.0 mL and analysed using a Carlo Erba 4300 GC instrument, equipped with FID and a wide bore PS264 column (25 m × 0.53 mm, film width 2 μm), using 1-octanol as internal standard. Tentatively identifications were performed by using a Hewlett–Packard GCD 1800A System, equipped with a capillary HP5 column (30 m × 0.25 mm, film width 0.25 μm), comparing the obtained MS spectra with those reported in the library of the instrument.

X-ray diffraction analyses were carried out using a Philips PW 1050/81 diffractomer (40 kV, 25 mA) equipped with a PW 1710 unit, and a Cu Kα radiation ($\lambda = 0.154118$ nm). A 2θ range from 10° to 80° was investigated at scanning rate of 0.10 °/s.

The TPD analyses were carried out using a ThermoQuest Catalytic Surface Analyser TPD/R/O 1100. The instrument detector was a TCD. The samples were pre-treated under He to 673 K, 10 °C/min, for 60 min. Then the samples were treated to 333 K with CO_2 (5% in He), 40 mL/min, for 20 min then they were treated to 333 K for 60 min. Finally the samples were treated from 333 to 673 K 10 °C/min for 60 min.

3. Results and discussion

The XRD power patterns of the precursors showed the presence of HT phases only while after calcination at 723 K XRD profiles (Fig. 2(a) and (c)) were those typical of non-stoichiometric MgO-type mixed oxide, while for the sample with Mg/Al atomic ratio = 4.0 traces of stoichiometric $MgAl_2O_4$ were detected and the peaks of the MgO-type phase evolved toward the typical values of stoichiometric MgO [21]. The rehydration step at room temperature gave a rise to a significant increase of crystallinity for all the samples (Fig. 2(b) and (d)), furthermore, for the sample with Mg/Al atomic ratios = 2.5 also the partial reconstruction of the HT structure was evidenced. This latter effect was almost absent in the sample with Mg/Al atomic ratio = 4.0, in which, of the contrary, both the segregation of the stoichiometric $MgAl_2O_4$ and the evolution of the mixed oxide towards stoichiometric MgO increased.

The TPD analyses of the samples after rehydration showed significant differences in the basicity between the samples with Mg/Al = 2.5 or 4.0. In particular, the former sample (Mg/Al = 2.5) showed a more intense peak at 423 K which is attributable to the desorption of weekly bonded CO_2, probably involved in the partial reconstruction of HT structure, another peak at 623 K which is attributable to the desorption of CO_2 bonded on strong basic sites. A peak which was fully absent in the sample with Mg/Al = 4.0. These data suggest that the partial segregation of $MgAl_2O_4$ and the corresponding evolution of mixed oxide phase toward the stoichiometric MgO, worsened the surface basicity in spite of the higher Mg/Al ratio. Condensation reaction of aromatic aldehydes with ketones may be catalysed by either bases or acids, the rates of acid-catalysed reactions usually being smaller than those of base-catalysed ones. Role of the base is to form an anion of the carbonyl compound, while the acid helps the enolization process of the ketone and activate the aldehyde by the protonation of carbonyl groups and/or accelerates the formation of arylidene derivatives. The five aromatic aldehydes investigated contained a carbonyl group with decreased electrophilicity in comparison to the C=O group in formaldehyde, due to its conjugation with the aromatic ring. Fluor-benzaldehydes, with fluorine atom in different positions, were chosen to see if electronic

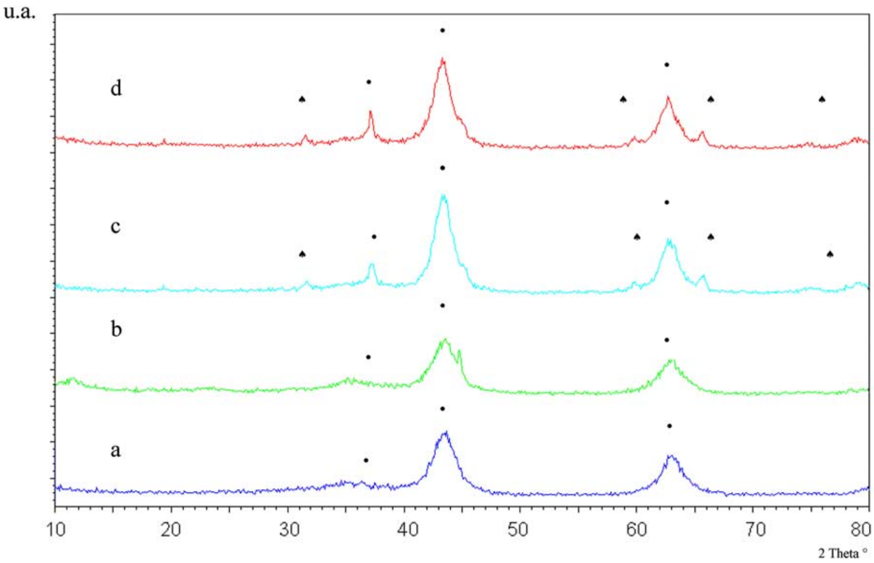

Fig. 2. XRD patterns of HT precursor: (a) Mg/Al = 2.5 after calcination at 723 K for 8 h; (b) Mg/Al = 2.5 following rehydration at room temperature for 7 h; (c) Mg/Al = 4.0 after calcination at 723 K for 8 h; (d) Mg/Al = 4.0 following rehydration at room temperature for 7 h, (♠) Reflexes of $MgAl_2O_4$ (●) Reflexes of MgO.

effects of the substituent affected the reaction in the same way observed with homogeneous catalysts. Finally, 2-naphthaldehyde is much more hydrophobic than benzaldehyde. The reaction of an aromatic aldehyde and a ketone is usually feasible. In fact there is poor competition from ketone condensing with itself and, by using an excess of ketone, it is possible to reduce both the formation of bis-arylidene compounds and the possible competition of some side reactions of the aromatic aldehyde like Canizzarro or Tishchenko reactions. The first reaction step is the enolate-anion formation: HT catalysts, having a wide spectrum of basic sites [22,23], may easily perform the acetone deprotonation. Enolate-anions further enter addition reactions to C=O groups, either of aromatic aldehyde or non-deprotonated acetone. The first C=O group is more electrophilic and, therefore, this is the main reaction pathway leading to β-hydroxy-ketone formation (Fig. 1, compound 3). However, the addition of enolate anions to acetone molecules always takes place, with the side formation of 4-hydroxy-4-methyl-2-pentanone. Finally, β-hydroxy-ketone may easily give rise to dehydration reactions, mainly by increasing the reaction temperature, with formation of arylideneacetone (Fig. 1, compound 4); the dehydration reaction that occurs spontaneously upon heating, however, is an acid catalysed one and the HT catalyst contain also Lewis acid sites, due to the presence of Al^{3+} ions in their structure [1,2,24].

The catalytic tests were carried out in first-order reaction conditions, since acetone was significantly in excess (molar ratio aromatic aldehyde/acetone of about 1:40) and acted as a reagent and solvent. Activated HT catalysts were powerful catalysts and the reaction usually reached conversion of the aromatic aldehyde = 85% in 2 h ca. (Fig. 3(a)), with a weak but not negligible effect of the reaction temperature. The reaction temperature had a significant influence on the second step of the reaction, with water elimination from aldol product and the formation of arylideneacetone, which was significantly lower at 273 K (Fig. 3(b)).

The presence and nature of substituents on the aromatic ring certainly influence the electronic density of carbonyl group. In fact, the conversion rate of the aldehydes investigated showed the following order: *meta*-F-benzaldehyde > *para*-F-benzaldehyde ≈ *ortho*-F-benzaldehyde > benzaldehyde > 2-naphthaldehyde (Fig. 4). Fluorine atoms introduced opposite inductive and mesomeric effects on the aromatic ring, the inductive effect being usually more relevant than the mesomeric effect. Therefore, according to expectations, the fluorinated benzaldehydes react more rapidly than benzaldehyde; the highest reactivity of meta-isomer could be explained by a highest dipolar moment that may favour the interaction with heterogeneous catalyst. The dipolar moments were calculated by using Alchemy software, with two calculation packages, after geometry optimisation (MOPAC and MM4). Finally the lower reactivity of the 2-naphthaldehyde should be due either electronic or steric effects, although the former should be predominant.

One relevant characteristic of HT catalysts is the Mg/Al atomic ratio that determines their basicity [1,2, 21–24]; thus different ratios in the typical range of pure HT compounds [1,2] have been investigated (Fig. 5). The best conversion values were obtained with the Mg/Al HT catalyst with Mg/Al atomic ratio = 2.5, in spite of the fact that the HT catalyst with atomic ratio Mg/Al = 4.0 contained more Mg^{2+} ions and, therefore, more

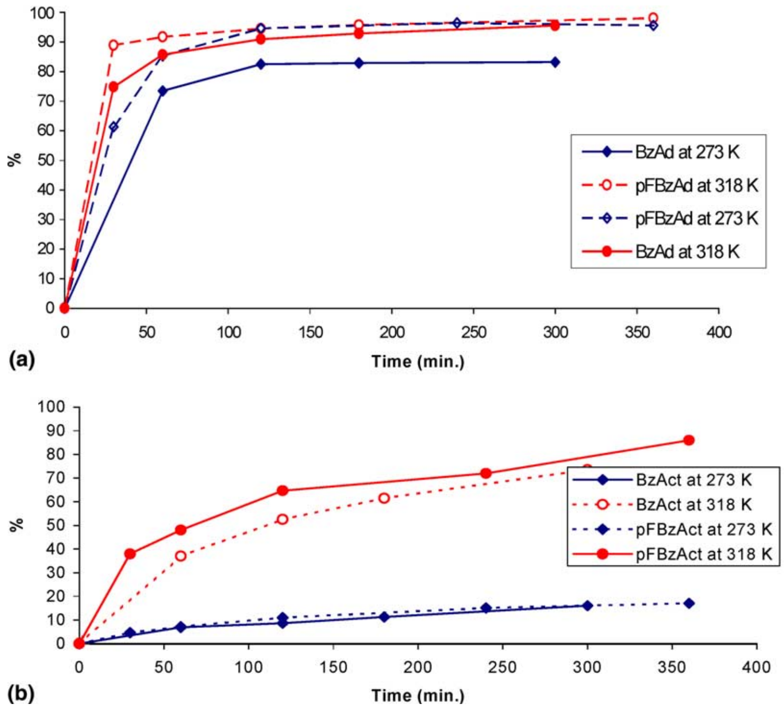

Fig. 3. Conversion (a) of benzaldehyde (BzAd) and *para*-fluorobenzaldehyde (pFBzAd) and yield (b) in benzylideneacetone (BzAct) and *para*-fluorobenzylideneacetone (pFBzAct) at different reaction temperatures.

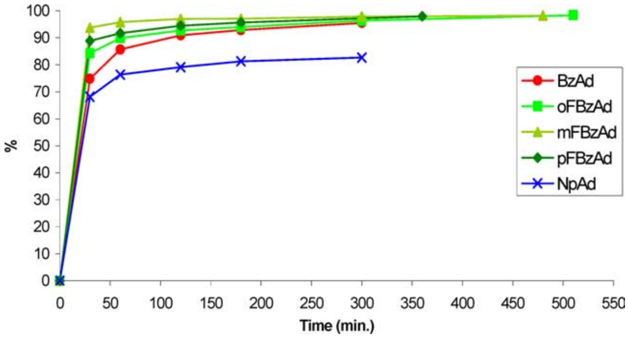

Fig. 4. Conversion of benzaldehyde (BzAd), *ortho*, *meta* and *para*-F-benzaldehydes (FBzAd) and naphthaldehyde (NpAd) at 318 K.

active base sites. It is noteworthy that Zn/Al or Ni/Al HT catalysts, with M/Al atomic ratio = 2.5, did not show any significant activity, in agreement with their lower basicity [1,2]. On the basis of fact that the aldolic reaction is equilibrium with a fine tuning demand of the experimental conditions, it is possible that an excess of base sites may favour the cleavage of hydroxy-ketones with an apparent result of slower conversion. Thus, three factors have been detected, which affect the condensation rate and the distribution of products: temperature, reaction time and Mg/Al atomic ratio.

The main reaction products of aromatic aldehydes with acetone were aldol (at lower temperatures and reaction times) and *trans*-arylideneacetone. The reaction mixture also contained some by-products as,

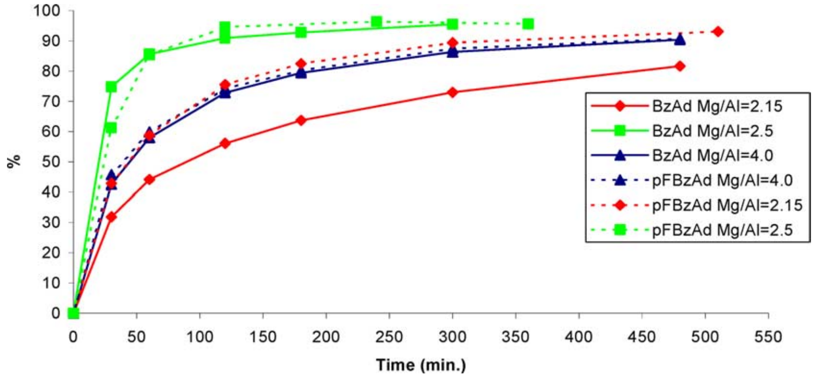

Fig. 5. Role of the Mg/Al atomic ratio on benzaldehyde and *p*-fluorobenzaldehyde conversion.

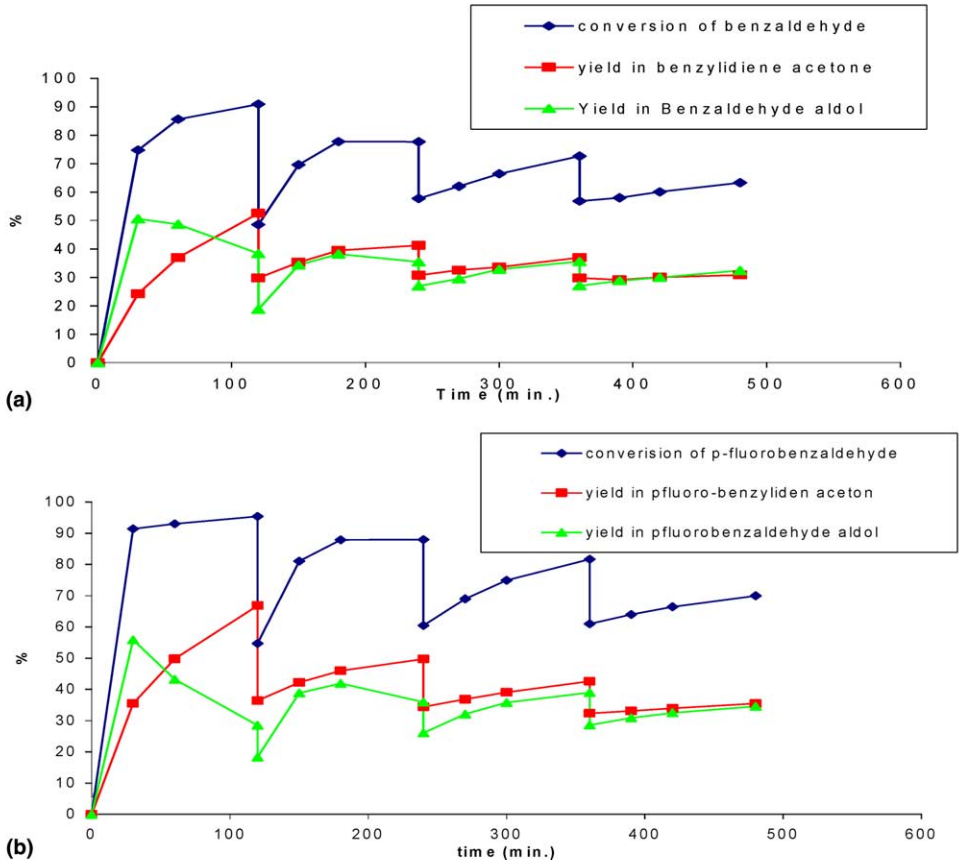

Fig. 6. Conversion values in the semi-continuous tests at 318 K feeding (a) benzaldehyde and (b) *para*-fluorobenzaldehyde.

cis-arylideneacetone, 1,3-diarylideneacetone and the self-condensation product of acetone (4-hydroxy-4-methyl-2-pentanone), for a total amount always <10% even after 8 h reaction at 318 K. These compounds were simply separated from the main product by re-crystallisation.

The investigated HT catalysts were very sensitive to traces of organic acids in the reaction mixture and aromatic aldehydes usually contain small amounts of corresponding acids, even if they are new or stored in well closed bottles. The acids may stop the condensation reaction likely adsorbing irreversibly on the base sites of HT catalysts. However, before the use a simple extraction with 10 wt% solution of Na_2CO_3 and subsequent dehydration with anhydrous Na_2SO_4 allowed to ward off this drawback.

Nowadays, the condensation reactions reported in literature are limited to a single cycle, with a large excess of the HT catalyst in comparison to the aldehyde [18]. Furthermore, an increase of the ratio benzaldehyde: HT catalyst gave rise to full deactivation of the catalyst due to the block of active sites by benzaldehyde adsorption. These conditions are very far from those required by a possible industrial application, thus it was investigated the possibility of setting-up a semi-continuous reaction, by repeated addition of fresh aldehyde, whenever most of it had already been transformed. Thus, in our tests new amounts of aldehyde were added after conversion of about 80%, with very positive results regardless of the nature of the aldehydes used (Fig. 6(a) and (b)). Such procedure changes the single application of HT catalysts into a semi-continuous process, provided that the oxidation of the aldehyde to the corresponding acid is fully avoided. In fact, the slight decrease of conversion observed may be mainly attributed to this problem.

4. Conclusions

Activated Mg/Al HT catalysts may efficiently replace homogeneous catalysts in condensation of aromatic aldehydes with acetone. This application gives rise to interesting activities, regardless of the nature of aldehydes fed. High reaction temperatures and reactions favoured the formation of arylideneacetone, while a Mg/Al = 2.5 (as atomic ratio) provided the best catalytic performances. Finally, the semi-continuous addition of the aromatic aldehyde during the process allowed a significant increase in the productivity per kilogram of catalysts, if the possible oxidation of aldehyde to the corresponding acid has been carefully avoided.

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