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The aldol condensation of acetaldehyde and heptanal on hydrotalcite-type catalysts

Didier Tichit,[a,*] Doina Lutic,[a,1] Bernard Coq,[a] Robert Durand,[a] and Rémy Teissier[b]

[a] *Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, UMR 5618 CNRS-ENSCM, 8, Rue Ecole Normale, 34296 Montpellier cedex 5, France*
[b] *ATOFina, CRRA, Rue Henri Moissan BP 63, 69310 Pierre-Bénite cedex, France*

Abstract

The aldol condensation of acetaldehyde and heptanal has been carried out in the liquid phase between 353 and 413 K using different types of solid base catalysts: MgO with strong Lewis basic sites, Mg(Al)O mixed oxides with acid–base pairs of the Lewis type obtained from hydrotalcite precursor, and rehydrated Mg(Al)O mixed oxides with Brønsted basic sites. The influence of several reaction parameters, temperature, acetaldehyde to heptanal molar ratio, nature of solvent (hexane, toluene, ethanol), has been investigated. A comparative study of the catalysts has been performed in the such defined optimal reaction conditions, i.e., 373 K, acetaldehyde/heptanal molar ratio, 2/1; and ethanol/reactants molar ratio, 5/1. Mg(Al)O mixed oxides calcined below 673 K are the most selective catalyst to 2-nonenal, the cross-condensation product formed when in the first step proton abstraction occurs from acetaldehyde. Acid–base pairs of moderate basic strength are suitable when this cross-condensation is the desired reaction. Stronger Lewis basic sites of MgO or Brønsted-type basic sites of the rehydrated mixed oxide tend to favor the formation of carbanion from heptanal. This latter leads to the formation of 2-pentyl-2-butenal and 2-pentyl-2-nonenal by cross-condensation with acetaldehyde and self-condensation, respectively.
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1. Introduction

Reactions involving C–C bond formation are of utmost importance for obtaining many fine chemicals of commercial interest. The base-catalyzed aldol condensation, which belong to this type of reaction is indeed very useful for the preparation of higher molecular weight aldehydes and/or ketones from lower easily available homologs. The exciting possibility of carrying out these reactions through a heterogeneous catalytic process can now be contemplated by taking advantage of the increasing number of available materials with finely tunable basicities. This is particularly the case of the hydrotalcite-type catalysts which have recently attracted much attention for various base-catalyzed reactions in fine chemistry [1]. Hydrotalcite-like compounds of general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{n-}_{x/n}] \cdot m H_2O$, also de-

nominated layered double hydroxides or anionic clays, constitute a class of compounds with positively charged layers and exchangeable anions in the interlayer space [2–4]. The structure is similar to that of brucite $Mg(OH)_2$, where Mg^{2+}-centered octahedra are linked by the edges to form infinite sheets. In the natural mineral hydrotalcite, whose name has been extended to this family of materials, some Mg^{2+} are isomorphously substituted for Al^{3+} and the formal positive charge thus appearing in the hydroxyl layers is usually compensated by carbonates linked by hydrogen bonds to water molecules. Dehydroxylation takes place and volatile anions are decomposed upon calcination, leading to mixed oxides. These materials obtained from hydrotalcite are the catalysts most largely used until now, though interest in activated hydrotalcites obtained by rehydration of the mixed oxides is growing. Using hydrotalcite-like catalysts, attractive results have been thus reported in: (i) the self-condensations of acetone [5–7], acetaldehyde [8], or butyraldehyde [9]; (ii) the condensation between aromatic aldehydes like benzaldehyde or substituted benzaldehydes and acetone [10],

substituted acetophenones [11,12], and heptanal [13]; and (iii) the condensations of acetone and citral [14,15].

However, the field of cross-condensation between linear aliphatic aldehydes to yield longer linear aldehydes was not explored till now despite the great interest of high-molecular-weight aldehydes as valuable monomers in some polymerization processes. It is worth noting the very challenging aspect of this proposal because various self- and cross-condensations can occur simultaneously. It was therefore the aim of this work to perform the aldol condensation of acetaldehyde and heptanal toward 2-nonenal, with catalysts obtained from hydrotalcite materials, as a model reaction of chain lengthening between aldehydes of close reactivities.

The catalysts were Mg(Al)O mixed oxides obtained from calcination at various temperatures of an Mg/Al hydrotalcite precursor, and the rehydrated form of these calcined materials. The main advantage of the hydrotalcites as catalysts comes from the opportunity to control to a certain degree their acido-basic properties [13,16]. The thermal decomposition in the range 623–823 K results in the formation of a Mg(Al)O mixed oxide with both strong Lewis basic and mild Lewis acid sites. The former are due to the presence of oxygen atoms of low coordination, and the latter to Al^{3+} cations. Rehydration of these calcined hydrotalcites allows the reconstruction of the lamellar structure owing to its memory effect. The counteranions in the interlayer space then become OH^-; the basic Lewis sites are thus moving to hydroxyls species which are Brønsted sites [5]. At the same time, the mild acidity of the mixed oxides disappears. This material is called meixnerite. The different nature of the active sites in the mixed oxides, on one hand, and the rehydrated samples, on the other hand, has been illustrated by the activities and selectivities reached in different reactions demanding specific types of sites. The rehydrated materials are the most active in the aldol condensations alone. They are thus very selective toward diacetone alcohol in the self-condensation of acetone [5], or toward 4-hydroxy-4-phenylbutan-2-one and pseudoionone in the condensations of benzaldehyde and acetone [17], and of citral and acetone [14], respectively. Lower selectivities are obtained with the mixed oxides because dehydration of the aldol, self-condensations reactions of the reagents, and oligomerizations may occur. Mixed oxides are in contrast highly active and selective in the Meerwein–Pondorf–Verley (MPV) reduction of aldehydes and ketones requiring Lewis-type sites only [18].

It was therefore interesting to compare the catalytic performances of mixed oxides obtained by calcination at different temperatures of an hydrotalcite precursor and of the rehydrated forms in the condensation of acetaldehyde and heptanal. The reaction will be also performed with MgO and rehydrated MgO whose efficiencies in aldolization have been put in evidence previously [19].

2. Experimental

2.1. Material preparation

The Mg–Al hydrotalcite was synthesized by coprecipitation of a gel at constant pH under air. With this aim 250-cm³ aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$, and $Al(NO_3)_3 \cdot 6H_2O$ (Mg/Al =3) was delivered into a polypropylene reactor by a chromatography-type pump at a constant flow of $1 \text{ cm}^3 \text{ min}^{-1}$. A second aqueous solution of 2 M NaOH + 0.5 M Na_2CO_3 was simultaneously fed by a pH-stat apparatus (718 Stat Titrino, Metrohm). The careful control of the flow maintained the pH during precipitation in the reactor at a constant value of 10.0 ± 0.2. After completion of the precipitation, the resulting suspension was aged at 353 ± 5 K for 15 h with stirring. The solid thus obtained was then isolated by centrifugation, washed thoroughly with deionized water, and dried overnight in oven at 353 K.

The exchange of nitrate anions was performed by dispersing 2 g of the as-synthesized hydrotalcite in a 1.5×10^{-3} M Na_2CO_3 solution under magnetic stirring at 353 K for 2 h. After filtration the solid was washed and dried in an oven at 353 K. This material will be hereafter referred as HT. The chemical analysis gives the formula $[Mg_{0.75}Al_{0.25}(OH)_2]^{0.25+}[CO_3^{2-}]_{0.125} \cdot mH_2O$, well consistent with the composition of the synthesis solution.

The Mg–Al mixed oxides were obtained by calcination of HT at the desired temperature (from 643 to 823 K) for 4 h in a dry synthetic air flow (mass, 2 g; flow, 100 cm³ min⁻¹; ramp, 1 K min⁻¹). These samples were hereafter labeled as HTc(673) for HT calcined at 673 K, for instance.

The rehydration of the mixed oxides to yield the meixnerite was carried out in situ after calcination. The sample was cooled to room temperature in synthetic air flow (CO₂ free), and then contacted with a flow (100 cm³ min⁻¹) of N₂ saturated with the vapor pressure of water at the same temperature (16 h for 1 g of sample).

A commercial Mg(Al)O mixed oxide, labeled KW 2200, was purchased from Kyowa. This sample has a molar ratio Mg/Al = 2.12 and a specific surface area of 160 m² g⁻¹ after activation at 723 K.

MgO was obtained by thermal treatment of Mg(OH)₂ (Strem Chemicals) at 673 K following the same procedure as described above. The rehydration process from MgO back to Mg(OH)₂ was conducted as well.

2.2. Characterizations

Chemical analyses of the as-prepared solids were performed at the Service Central d'Analyse du CNRS (Solaize, France) by ICP-MS.

XRD powder patterns were collected on a CGR Theta 60 instrument using monochromatized Cu-K_{α_1} radiation ($\lambda = 0.15401$ nm, 40 kV, and 50 mA).

BET specific surface areas were determined by N₂ adsorption at 77 K with a Micromeritics ASAP 2000 apparatus

on samples calcined at 723 K and outgassed at 523 K and 10^{-4} Pa.

The basicity of the calcined samples was studied by CO_2 adsorption followed by calorimetry and gravimetry using a Setaram TG-DSC-111 apparatus. The samples were previously outgassed at 723 K, cooled to 373 K, and contacted with flowing CO_2.

The acidity of the calcined samples was estimated from temperature-programmed desorption of NH_3 (NH_3-TPD) using a conductivity cell for the detection of the effluent gases. The samples were previously outgassed at 723 or 873 K in some cases, cooled to 373 K, and contacted with NH_3 vapor. After the sample was purged, the temperature was increased to 723 K (ramp: 10 K min^{-1}), and evolved ammonia was trapped in a HCl solution and finally titrated.

2.3. Catalytic tests

The reaction between acetaldehyde ($+95\%$, Aldrich) and heptanal ($+98\%$, Aldrich) was performed in liquid phase in a sealed stainless-steel autoclave (100 mL), equipped with mechanical stirring and sampling device. Usually, about 70% of the solvent (ethanol, $+95\%$, Carlo Erba), the internal standard (decane, $+98\%$, Fluka), and 2 g of the catalyst previously activated and kept under dry synthetic air flow at room temperature were poured in the autoclave before closing. The reactor was purged for 1 min with N_2 flow, pressurized at 2×10^5 Pa, and then heated at the reaction temperature. Typically the solution containing 0.07 mol of heptanal and 0.14 mol of acetaldehyde in a volume of solvent necessary to reach a total volume of 80 mL was introduced in the autoclave with a pump, as soon as the reaction temperature was reached. The reaction mixture was analyzed periodically by gas chromatography on a Hewlett Packard HP 4890 machine, equipped with a capillary HP-5 column (30 m length, 0.32 mm i.d.), using decane as internal standard. The products were first identified by a gas chromatograph HP 5890 coupled with a mass spectrometer. Expression of results:

Reactant conversion (mol%) $= 100 \times$ (reactant$_{in}$ − reactant$_{out}$)/reactant$_{in}$;

Selectivity to product i = (mole of reactant converted to i)/(total number of mole of reactant converted).

3. Results and discussion

3.1. Characterization of the materials

The calcination at temperature T (643–823 K) of the hydrotalcite precursor HT leads to the materials HTc(T). All present typical XRD patterns of the Mg(Al)O phase (Fig. 1). These mesoporous materials exhibit very similar specific surface areas (220–240 m^2 g^{-1}) and pores of 60 nm mean size, whatever the calcination temperature (Table 1). After rehydration of HTc(643) and HTc(673) mixed oxides, the
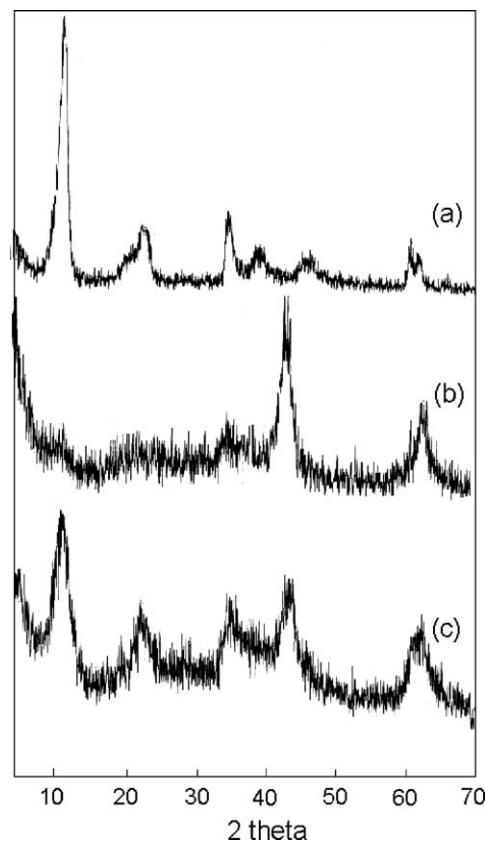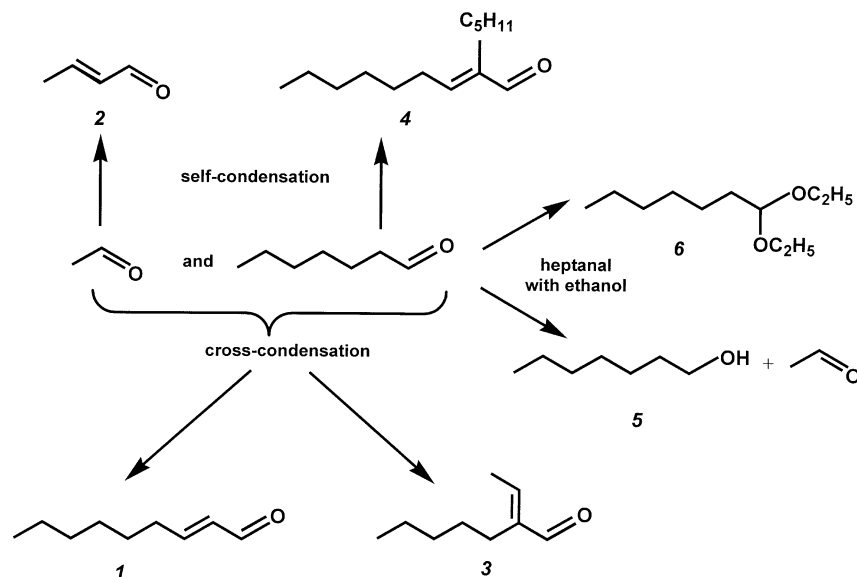

Fig. 1. XRD powder patterns of HT (a), HTc(673) (b), and HTc(673)R (c).

XRD patterns show that the lamellar structure is present in HTc(643)R and HTc(673)R (Fig. 1).

In order to further explain their catalytic behavior the acido-basic properties of the catalysts have been characterized by CO_2 and NH_3 adsorptions and TPD experiments. The heat of CO_2 adsorption is considered as a measure of the strength of basic sites. The strength of the acid sites is evaluated from the temperature of maximum desorption rate of NH_3 (T_{max}). The number of basic (N_{base}) and acid sites (N_{acid}) are determined from the amounts of CO_2 in TG-DSC and NH_3-TPD experiments, respectively. The results are reported in Table 1. MgO which exhibit sites of the higher basic strength and a low amount of acid sites behave therefore as a strong basic solid. Regarding the mixed oxides calcined in the range 643–823 K, they are characterized by

Table 1
Some characteristics of the texture, acid, and basic properties of the catalysts

Catalysts	N_{base} (meq g^{-1})	$\Delta H(CO_2)$ (kJ mol^{-1})	N_{acid} (meq g^{-1})	T_{max} in NH$_3$-TPD (K)	N_{base}/N_{acid}	Surface area (m^2 g^{-1})
HTc(643)	0.15	−65	0.32	–	0.47	217
HTc(673)	0.27	−61.5	0.29	543	0.93	225
HTc(723)	0.46	−73.5	0.15	548	3.07	238
HTc(823)	0.47	−78	0.10	548	4.70	224
MgO	1.03	−83	0.06	548	17	160

Scheme 1. Simplified scheme of the reaction of acetaldehyde and heptanal on a solid basic and acid catalyst.

the presence of acid–base pairs, as expected. These data call for two comments:

1. There is a net increase of basic strength with the temperature of calcination. In contrast, the acid strength remains almost constant in all the temperature ranges investigated.
2. There is a threefold increase of the number of basic sites while that of acid sites decreases to the same extent when the calcination temperature goes from 643 to 823 K.

Two distinct behaviors could actually be identified for the mixed oxides. Upon calcination below 673 K, a medium basic strength with $-\Delta H(CO_2)$ not exceeding 65 kJ mol^{-1} and ratios $N_{base}/N_{acid} < 1$ show that they behave as moderately basic solids. The basic character is magnified for calcination at temperature above 673 K.

3.2. The reaction scheme

The reactions between acetaldehyde and heptanal involve self- and cross-condensations (Scheme 1). The selectivities can thus be expressed with respect to products coming from either heptanal or acetaldehyde conversion. This is illustrated in Fig. 2 for the reaction carried out on HTc(673) at 393 K. With respect to heptanal conversion (Fig. 2a), 2-nonenal (**1**) and 2-pentyl-2-butenal (**3**, mixture of the *E* and *Z* isomers) are the main products from cross-condensations. The self-condensation of heptanal leads to 2-pentyl-2-nonenal (**4**, mixture of the *E* and *Z* isomers) which amounted to 20% after 3 h reaction. The formations of heptanol (**5**) and diacetal (**6**) from secondary reactions also take place to a lower extent. Heptanol comes from the MPV reduction of heptanal by hydrogen transfer from ethanol. This reaction has already been reported as catalyzed by Mg(Al)O
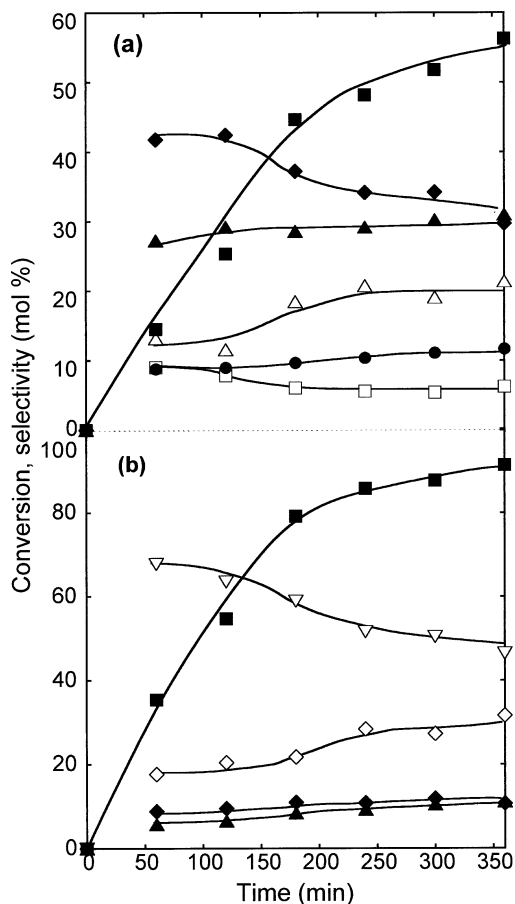

Fig. 2. Conversion and selectivity to the different products as a function of time in the reaction of acetaldehyde and heptanal on HTc(673) catalyst; results given on an heptanal conversion basis (a), and acetaldehyde conversion basis (b); (■) heptanal or acetaldehyde conversion, (◆) **1**, (▽) **2**, (▲) **3**, (△) **4**, (●) **5**, (□) **6**, and (◇) oligomers from self-condensation of acetaldehyde. Conditions: solvent, ethanol; ethanol/reactants molar ratio, 5; $T_{reaction} = 393$ K; acetaldehyde 0.14 mol and heptanal 0.07 mol, 2 g catalyst.

mixed oxides [18]. The diacetal comes from the condensation of heptanal and ethanol on acid sites. Selectivities toward both compounds were in the range 5–10%. It is worth noting the changes of selectivity when the conversion goes on. The selectivity to **1** decreases whereas those toward **3** and **4** increase. In Fig. 2b the results were reported with respect to acetaldehyde conversion. Compared to the data determined on an heptanal conversion basis, one should note (i) the larger conversion of acetaldehyde as compared to heptanal, (ii) the lower selectivities to **1** and **3** (almost 10%), and (iii) the decrease of selectivity when the conversion goes on of 2-propenal (crotonaldehyde, **2**), the product of acetaldehyde self-condensation.

For the sake of comparison, the reaction was carried out under the same conditions and using 10^{-4} mol NaOH as homogeneous catalyst. The reaction rate was faster but the selectivity to **1** very low ($< 10\%$); the main products were crotonaldehyde and oligomers from the self-condensation of acetaldehyde.

The aldol condensation on basic sites occurs in the first step by the abstraction of an hydrogen atom at the α position of the carbonyl group of the aldehyde leading to a carbanion species. In a second step the aldol is formed by reaction of the carbanion on the carbonyl group of an other aldehyde molecule. Generally the aldol is dehydrated on the weak acid sites of the catalyst giving the α, β-unsaturated aldehyde. When two different aldehydes are concerned, four products resulting from self- and cross-condensation reactions could be obtained.

The cross-condensation of acetaldehyde and heptanal leading to **1** results from the attack of the acetaldehyde carbanion by heptanal (Scheme 2). However, the attack of this
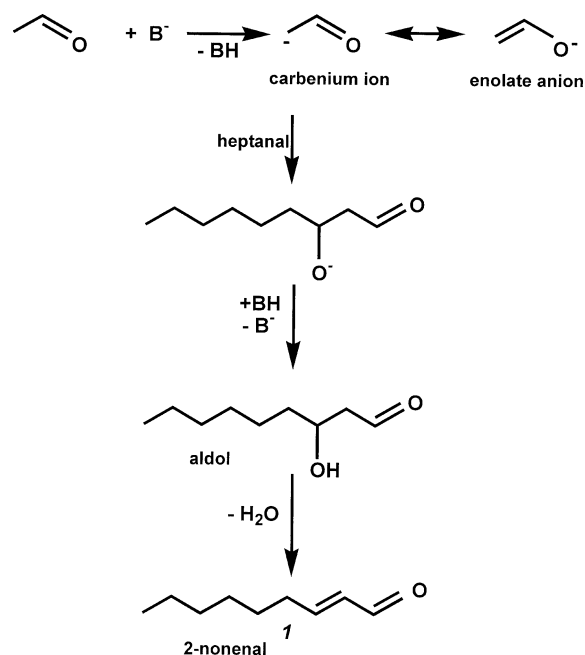
Scheme 2. Cross-condensation between the carbanion of acetaldehyde and heptanal.
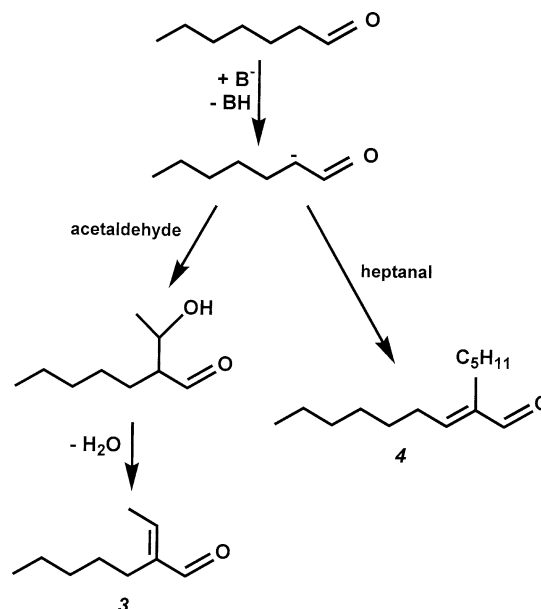
Scheme 3. Cross- and self-condensation from the carbanion of heptanal.

carbanion by a second acetaldehyde molecule leads to the C_4 aldol which is then dehydrated to **2** on acid sites. In contrast when the carbanion was formed from heptanal, its cross-condensation with acetaldehyde leads to **3**, whereas **4** results from the self-condensation with an other heptanal molecule (Scheme 3).

Assuming an equal probability for the formation of carbanions from acetaldehyde or heptanal, and a close reactivity of those with aldehydes, the selectivities to **1**, **3**, and **4** should be 25, 25, and 50%, respectively, with respect to heptanal conversion. One should emphasize in the present case the close reactivity of the two aldehydes which makes the achievement of a high selectivity in one product much more challenging. It is worth noting that on HTc(673) (Fig. 2a), the selectivity to **1** amounted up to ca 43% at low conversion, and even more regarding the products from the aldol condensation alone (ca 51%). The selectivity to **1** decreases when the reaction goes on due to the faster consumption of acetaldehyde than heptanal. The relative coverage by heptanal of the catalyst surface then increases which favors the self-condensation to **4** (Fig. 2a). An improvement of the selectivity to **1** may result from the adjustment of the reaction conditions, but also from tuning the acido-basic properties of the catalyst surface [15,20].

We have studied these two aspects by first carrying out a parametric study (reaction temperature, reactants molar ratio, solvent) on a commercial catalyst (KW 2000). Under the optimal reaction conditions thus defined, we then investigated the influence on the reaction of the acido-basic properties of the catalyst.

3.3. Parametric study

The influence of the reaction temperature on the selectivity to **1** is shown in Fig. 3 as a function of the heptanal
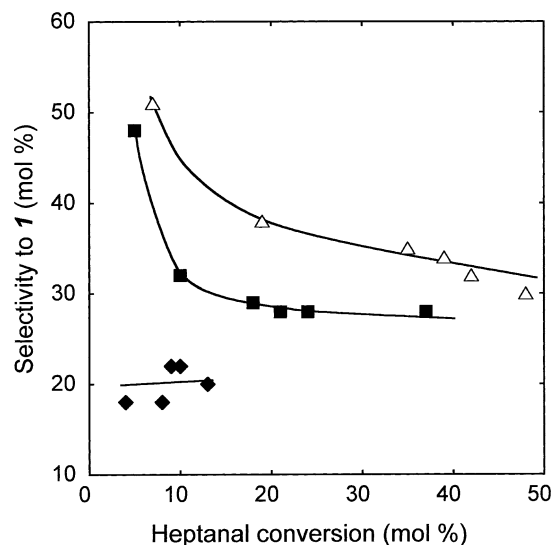
Fig. 3. Selectivity to **1** as a function of heptanal conversion in the reaction of acetaldehyde and heptanal at different reaction temperatures; (◆) 373, (■) 393, and (△) 413 K. Conditions: acetaldehyde/heptanal molar ratio, 2; solvent, ethanol; ethanol/reactants molar ratio, 5; catalyst, KW 2200.

conversion. No reaction proceeds below 373 K and the conversion remains below 13% with a selectivity around 20% at this temperature. The conversion and selectivity to **1** increase markedly with reaction temperature, and the latter reaches ca 40% at 413 K. However, at higher temperatures, several consecutive condensation reactions involving acetaldehyde occur leading to oligomers. Selectivity to **1** levels off in all cases above 10% conversion. An optimum reaction temperature of 393 K was then chosen to obtain good yields to **1** and to avoid problems arising from oligomer formation.

The selectivity toward cross- and self-condensation reactions was expected to strongly depend on the molar ratio between the two reactants in the reaction medium. Reactions with acetaldehyde/heptanal molar ratios (AA/HA) of 1, 2, and 4 were carried out at 393 K, with an ethanol/reactant molar ratio of 5. The selectivity to **1**, as a function of heptanal or acetaldehyde conversion, is reported in Fig. 4. A selectivity in the range of 30–65%, on an heptanal conversion basis (Fig. 4A), is obtained with a molar ratio AA/HA = 4. However, this selectivity becomes lower than 5% when expressed on an acetaldehyde conversion basis (Fig. 4B), due to the oligomerization of this reactant. The selectivity to **1** on a acetaldehyde conversion basis is of 8–14% for molar ratios AA/HA = 1 and 2; this is due to a lower extent of acetaldehyde oligomerization at low AA/HA ratio. Unfortunately, the selectivity to **1** then becomes lower than 20% on an heptanal conversion basis, for AA/HA = 1. We have thus considered a molar ratio AA/HA = 2 as a compromise to get good selectivity to **1** in the whole range of heptanal conversion.

Experiments were carried out at 393 K with AA/HA = 2 and toluene, hexane, or ethanol as solvent (solvent to reactants ratio of 5), previously used for condensation reactions with hydrotalcite-like catalysts [10,12,21]. A great differ-
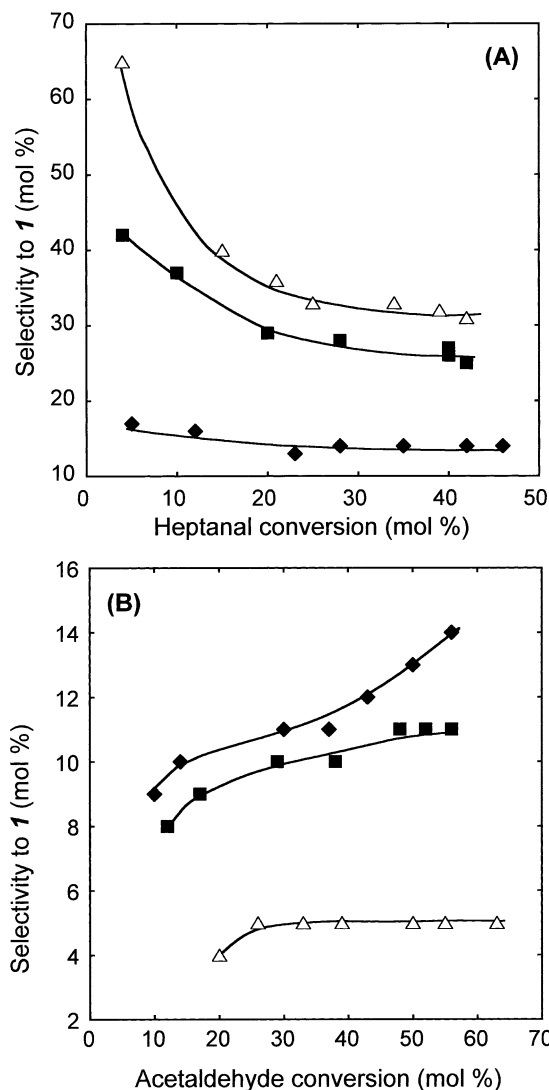

Fig. 4. Selectivity to **1** as a function of heptanal (A) and acetaldehyde (B) conversions in the reaction of acetaldehyde and heptanal at different acetaldehyde/heptanal molar ratios: (◆) AA/HA = 1, (■) AA/HA = 2, and (△) AA/HA = 4. Conditions: solvent, ethanol; ethanol/reactants molar ratio, 5; $T_{reaction}$ = 393 K; catalyst, KW 2200.

ence of reactivity was observed. After 8 h reaction, the heptanal conversion is in the range 20–25% with toluene or hexane, whereas it reaches 45% with ethanol. Lowering of the rates when Michael and Knoevenagel reactions were performed in hexane and toluene, respectively, has also been reported [10,21]. We may anticipate that ethanol, a highly polar solvent, improves the desorption of products from the surface of the catalyst. On one side it minimizes the self-condensations and other side reactions, and on the other side it increases the activity. The influence of the solvent/reactant ratio was then examined with ethanol. The selectivity to **1** increased and the conversion simultaneously decreased when this ratio goes from 2 to 10 (Fig. 5). These results accounted for the expected lowering of conversion and secondary self-condensation reactions when the coverage of the reactants at the surface decreased. The yield to **1** (with re-
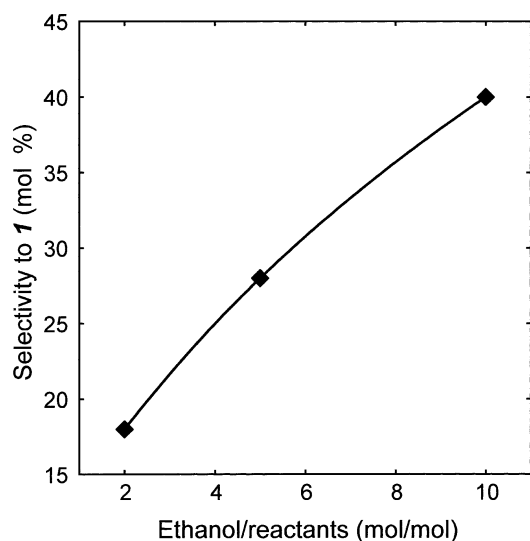
Fig. 5. Selectivity to **1** at different ethanol to reactants molar ratios and for an heptanal conversion of 30%. Conditions: acetaldehyde/heptanal molar ratio, 2; $T_{reaction}$ = 393 K; catalysts, KW 2200.

Table 2
Activities and selectivities (on an heptanal conversion basis) obtained in the reaction of acetaldehyde and heptanal on different catalysts (acetaldehyde/heptanal molar ratio, 2; $T_{reaction}$ = 393 K; solvent, ethanol)

Catalysts	Initial rate	Selectivity (%)[a]				
	(10^6 mol g^{-1} min^{-1})	**1**	**3**	**4**	**5**	**6**
HTc(643)	78	32	22	14	7	25
HTc(643)R	8.8	24	39	33	1	3
HTc(673)	86	41	29	14	9	8
HTc(673)R	70	39	36	22	3	1
HTc(723)	103	39	33	22	4	2
HTc(823)	130	35	41	23	4	0
MgO	320	17	40	39	2	1
Mg(OH)$_2$	66	38	37	23	1	0

[a] At conversion of 30%.

spect to heptanal) of ca 12% was actually constant above a solvent/reactants ratio of 5.

The heterogeneously base-catalyzed aldol condensation of aldehydes and ketones obeys a Langmuir–Hinshelwood-type kinetic model [12,17,22]. The selectivity to **1** is thus favored by a high interdispersion in the adsorbed layer of heptanal between activated acetaldehyde carbanions. From the above results this is achieved by: (i) a higher reaction temperature and a larger ethanol/reactants ratio which decrease the heptanal coverage, and (ii) a large AA/HA reactant ratio which favors the interdispersion of adsorbed heptanal in surrounding acetaldehyde. However, we have to pay attention to the yield and an excessive self-condensation of acetaldehyde. For these reasons we have chosen a temperature of 393 K and AA/HA and ethanol/reactants ratios of 2 and 5, respectively, as a good compromise for the reaction conditions.

Under these conditions we have then evaluated the opportunities which could be brought by the various hydrotalcite-based materials to modify the acido-basic properties of the surface, and in fine the respective activation of heptanal and acetaldehyde as carbanions.

3.4. Influence of catalytic materials

Initial reaction rates and selectivities obtained with the different catalysts are reported in Table 2. The initial rate increases slightly with the calcination temperature of the mixed oxide. The rehydrated materials are less active.

Interesting features call for several comments regarding the evolution of selectivity patterns. First of all, the presence of acid–base pairs in the HTc(T) catalysts well accounted for the products obtained. Compound **1** is obtained predominantly with HTc(T) calcined below 823 K. However, it is worthy to note that selectivities for **3** and **4** increase with the

calcination temperature and **3** becomes the most abundant product with HTc(823). This is also the case with MgO for which the selectivities to **3** and **4** both reach 40%, clearly higher than that to **1**. Significantly, as selectivities to **3** and **4** increase, that to **5** decreases. The MPV reduction of heptanal, accounting for the formation of **5**, occurs also to a lower extent in the case of the rehydrated mixed oxides The inhibition of the MPV reaction after rehydration is in line with the results previously reported by Kumbhar et al. [18]. They show that the synergetic effect between strong Lewis basic and mild acid sites of the mixed oxides is more suitable than the Brønsted-type sites of the rehydrated hydrotalcite for catalyzing this reaction.

Finally the formation of **6**, catalyzed by acid sites, decreases steadily with the calcination temperature of the mixed oxides, and this compound is almost absent on rehydrated materials, as well as on MgO and Mg(OH)$_2$.

It must be recalled that the formation of **1** on the one side, and of **3** and **4** on the other side, results in the first step from an α hydrogen abstraction from acetaldehyde and heptanal, respectively, to yield the carbanion. This hydrogen abstraction is expected to be easier as the length of the alkyl chain becomes shorter, i.e., for acetaldehyde in comparison to heptanal. Consistently, the mixed oxides calcined at or below 673 K, of moderate basicity, lead to **1** predominantly rather than **3** and **4**. In this case, the competitive formation of carbanions from acetaldehyde or heptanal is clearly in favor of the former. When the basic strength increases, i.e., for calcination above 673 K, the discrimination between acetaldehyde and heptanal for the formation of carbanions is less efficient. This behavior is put in evidence in Fig. 6 where the ratio **1**/(**1**+**3**+**4**) has been reported as a function of the heat of CO_2 adsorption. Accordingly, MgO which is strongly basic (Table 1) gives the largest amounts of **3** and **4**, coming from the heptanal carbanion. This behavior is quite similar to that observed in the synthesis of jasminaldehyde involving also heptanal [13], for which higher selectivity was obtained with the less basic catalyst (CsX); stronger basic catalysts (MgO and hydrotalcites calcined at high temperature) lead to high amounts of the self-condensation product of heptanal.
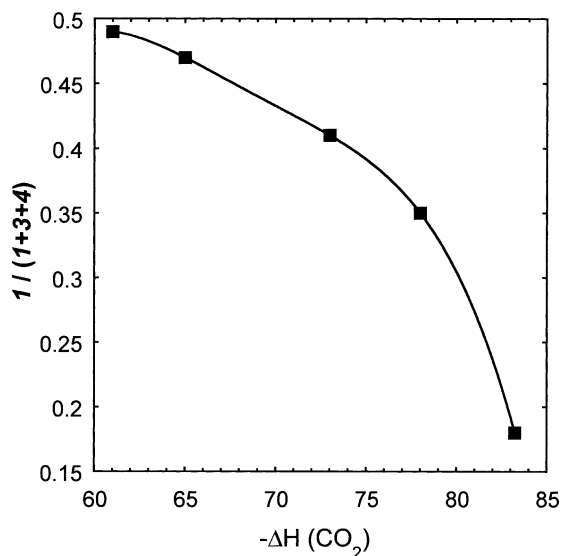
Fig. 6. Selectivity ratio **1**/(**1** + **3** + **4**) as a function of the enthalpy of CO_2 adsorption on the different catalysts.

Fig. 7. Selectivity to diacetal (**6**) as a function of N_{acid} in the different catalysts.

The rehydrated hydrotalcites possess Brønsted basic sites. In most studies these catalysts are more active and selective to the cross-condensation products than the mixed oxides [10,13–15,17,23]. Several explanations have been proposed for this behavior. From calorimetric experiments Rao et al. [17] reported a lower basicity of the surface after rehydration. They concluded that the improvement in activity accounted for a better specificity of OH^- for aldolization, Lewis basic sites O^{2-} working worse even if their basic strength is higher. Roelofs et al. [15,24] demonstrated that less than 5% of the total number of OH^- in the rehydrated samples is available for condensation reactions. However, they are highly active due to their localization at the edge of the reconstructed platelets of the layered structure. Otherwise, Climent et al. [13] suggested that the OH^- sites in the rehydrated samples are of medium basic strength and thus well adapted to the aldol condensation.

Our results in the condensation of acetaldehyde and heptanal show that the rehydrated hydrotalcites are less active but more selective for the self-condensation of heptanal than the mixed oxides. Brønsted OH^- sites thus appear less specific for this type of cross-condensation involving two linear aldehydes. It comes out that Lewis-type basic sites are more efficient, provided that they were of moderate strength in order to maintain the proton abstraction from heptanal, in competition with acetaldehyde, to a lower extent.

Finally, the selectivity to **6** increases with the number of acid sites in the catalysts, as expected (Fig. 7).

The maximum achieved yield to **1**, on an heptanal basis, was almost 21% (60% conversion and 35% selectivity) on HTc(673). To date, there is no report on the cross-condensation between aliphatic aldehydes to be compared. One can only note that in the cross-condensation between acetone and acetaldehyde to pent-3-en-2-one on nonzeolitic molecular sieves [25], the maximum yield, with respect to
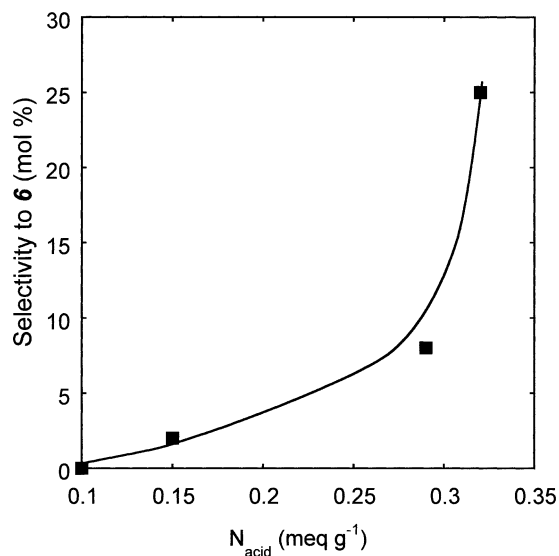
acetaldehyde, ranged between 16 and 40%. It is worth noting that such yields were achieved with a large excess of the less reactive acetone (acetone/acetaldehyde, 4/1). This is obviously inapplicable in the present study due to the very close reactivity of the two aldehydes.

4. Conclusions

The reaction of acetaldehyde and heptanal on catalysts elaborated from an hydrotalcite precursor (Mg/Al = 3) yields a wide variety of products. Most of them (usually more than 80%) originate from cross- and self-condensation of the aldehydes on basic and acid-pair sites. The most efficient material for the cross-condensation to 2-nonenal is Mg(Al)O calcined at 873 K. A maximum yield of 21% was reached at 393 K in ethanol as solvent and a moderate excess of acetaldehyde (acetaldehyde/heptanal, 2/1). This excess is necessary to achieve a good balance between both reactants in the adsorbed state and then to favor the cross-condensation.

From a practical point of view, one could conclude that the initial goal, the selective cross-condensation to produce 2-nonenal, was not achieved. This is due to the very close reactivity of acetaldehyde and heptanal to form the carbanion upon interaction with the basic surface.

However, from a fundamental point of view, a very interesting aspect deals with the high sensitivity of the aldehyde activation with the fine tune of surface basicity. Other things being equal, the acid–base pairs are the most efficient sites for this reaction, and the relative selectivity to **1**, in comparison to **3** and **4**, can suffer a fivefold increase when the strength of the basic sites are decreased. This is due to a preferential activation of acetaldehyde. In contrast, on solids of stronger basicity, there is no discrimination between the

abstraction of protons from acetaldehyde or heptanal by the basic sites; the latter leading to the formation of 2-pentyl-2-butenal.

Acknowledgment

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