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Condensation of aldehydes for environmentally friendly synthesis of 2-methyl-3-phenyl-propanal by heterogeneous catalysis

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Abstract

Eco-friendly synthesis in "one-pot" of 2-methyl-3-phenyl-propanal from benzaldehyde and propanal was studied using a multifunctional catalyst as an alternative to the three-step conventional process involving basic, acidic and hydrogenating catalysts. Mg(Al)O mixed oxides obtained from hydrotalcite precursor achieved the two first steps of condensation and dehydration. Addition of water to the solvent improves the activities and selectivities of Mg(Al)O, thanks to the reconstruction of the lamellar structure with OH^- as compensating anions, acting as Brønsted basic sites. Mg(Al)O was then used as support for a multifunctional catalyst impregnated with Pd. Pd/Mg(Al)O led to 45% dihydrocinnamaldehyde selectivity at 43% conversion in benzaldehyde in the "one-pot" process.

Keywords: 2-Methyl-3-phenyl-propanal; "One-pot" synthesis; Hydrotalcite; Palladium

1. Introduction

High molecular weight aldehydes and ketones are important chemicals usually prepared from condensation of short aldehydes or ketones in a three-step process consisting of a base-catalyzed aldol condensation, followed by the acid-catalyzed dehydration of the β-hydroxy-aldehyde or β-hydroxy-ketone, and finally with a selective hydrogenation of the α,β-unsaturated aldehyde. These operations in liquid phase generate high amounts of waste salts and effluents, explaining new trends towards the development of eco-friendly "one-step" processes using multifunctional heterogeneous catalysts. This approach has been extensively explored at the laboratory scale for the synthesis of methyl isobutyl ketone (MIBK) from acetone, using several types of Pd supported catalysts [1–3] or Pd-containing hydrotalcite-like compounds [4–6]. The "one-step" synthesis of higher molecular weight ketones are scarce in spite of their interest as fine chemicals; though the synthesis of 2-ethylhexanal from *n*-butyraldehyde [7], and the reactions of acetone with aliphatic or aromatic aldehydes [8,9] with Pd supported catalysts have been claimed. This work aimed at the "one-pot" synthesis of 2-methyl-3-phenyl-propanal, involving in the first step a condensation between propanal and benzaldehyde, using multifunctional catalyst obtained from Pd on basic support. Pd is known to promote hydrogenation of C=C bond conjugated to C=O bond. Basic oxides, like MgO, or alkaline exchanged zeolites would be useful supports for that purpose. However, layered double hydroxides (LDHs) or hydrotalcite-like compounds have shown interesting properties as precursors of acido-basic catalysts for the aldol and Knoevenagel condensations between acetone and

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benzaldehyde or substituted benzaldehydes [10–13]. But the condensation between higher aliphatic ketones and benzaldehydes using LDH has received less attention. Therefore, Na- and Cs-exchanged beta zeolites, MgO and Mg(Al)O mixed oxides obtained from a LDH precursor have been compared in the two first steps. Pd supported on the best support thus defined has been then used in the "one-pot" process.

2. Experimental

2.1. Sample preparation

The starting beta zeolite (BEA) was a CP 814 from PQ in the Na form (Si/Al = 12.5) further exchanged with $CsNO_3$. This sample calcined at 723 K will be thereafter noted NaCs-BEA. MgO was obtained by calcination at 723 K of $Mg(OH)_2$ (Strem Chemical). Mg/Al LDH (Mg/Al = 3) was prepared by coprecipitation at constant pH = 10 of the Mg and Al nitrate salts. The precipitated gel was then hydrothermally treated at 353 K for 17 h, filtered, thoroughly washed with H_2O and dried at 353 K. Mg(Al)O mixed oxide was obtained by calcination at 623 K of Mg/Al LDH. The Pd/Mg(Al)O sample was prepared by impregnation of Mg(Al)O with 0.2 wt.% Pd from Pd–acetylacetonate in toluene solution, then calcined in air at 623 K and reduced in hydrogen flow (H_2/N_2, 20/80) at 473 K.

2.2. Sample characterization

XRD powder patterns were collected on a CGR Theta 60 instrument using monochromatized Cu $K\alpha_1$ radiation. BET specific surface areas were determined by N_2 adsorption at 77 K on a Micromeritics ASAP 2100 on the samples outgassed at 523 K (10^{-4} Pa). The basicity of the calcined samples was studied by the adsorption and temperature-programmed desorption (TPD) of CO_2 with a Setaram TG-DSC-111 microcalorimeter. The samples were previously outgassed at 723 K, cooled to 373 K, and contacted with flowing CO_2. Thermal events and weight uptakes in the microcalorimeter cell were then recorded. TPD experiments were performed following the weight loss in He flow from 373 to 723 K after the CO_2 uptake (heating rate, 10 K min^{-1}). Total acidity was measured by TPD of NH_3. The samples were previously outgassed at 723 K, cooled to 373 K, and contacted with NH_3 vapor. After purging the temperature was increased up to 923 K (heating rate, 10 K min^{-1}) and evolved ammonia was trapped in a HCl solution followed by conductimetry and titrated.

2.3. Catalytic tests

The reactions were carried out in a 100 ml stirred stainless steel reactor (Parr) at 403 K under N_2 pressure (200 kPa) with 0.4 g of catalyst in 70 ml propanol or propanol/water (97/3). Propanal/benzaldehyde molar ratios ranged between 1.5 and 10 with a constant benzaldehyde concentration of 0.4 M. When the full "one-pot" process was performed (condensation + hydrogenation) the Pd/Mg(Al)O catalyst was reactivated in the batch reactor at 473 K under H_2 (3 MPa) in propanol/water (97/3). The reaction was carried out at 403 K under 1 MPa H_2 pressure. The reaction products were identified with GC–MS (HP 5970) and analyzed with a chromatograph (HP 4890) equipped with a Carbowax 20 M capillary column. Initial rates, conversion and selectivity were calculated relatively to benzaldehyde.

3. Results and discussion

3.1. Characterization of the samples

The chemical analysis of the as-prepared Mg/Al hydrotalcite giving the formula $[Mg_{0.75}Al_{0.25}(OH)_2][NO_3^-]_{0.25}\cdot mH_2O$, and the XRD pattern (Fig. 1) are consistent with a well-crystallized LDH structure. Both Mg(Al)O, obtained after calcination at 723 K of the Mg/Al precursor, and Pd/Mg(Al)O exhibit XRD patterns of mixed oxides. PdO lines are not detected in Pd/Mg(Al)O in agreement with its low Pd content. The specific surface areas increase from 80 to 230 $m^2\,g^{-1}$ when going from Mg/Al LDH to Mg(Al)O thanks to dehydration and decomposition of the anions. The specific surface area is slightly higher for MgO and nearly three times higher for NaCs-BEA reaching 680 $m^2\,g^{-1}$ (Table 1).

These samples present different acido-basic properties put in evidence by TPD of NH_3 and CO_2 z(Table 1). NaCs-BEA is poorly acidic and basic, but

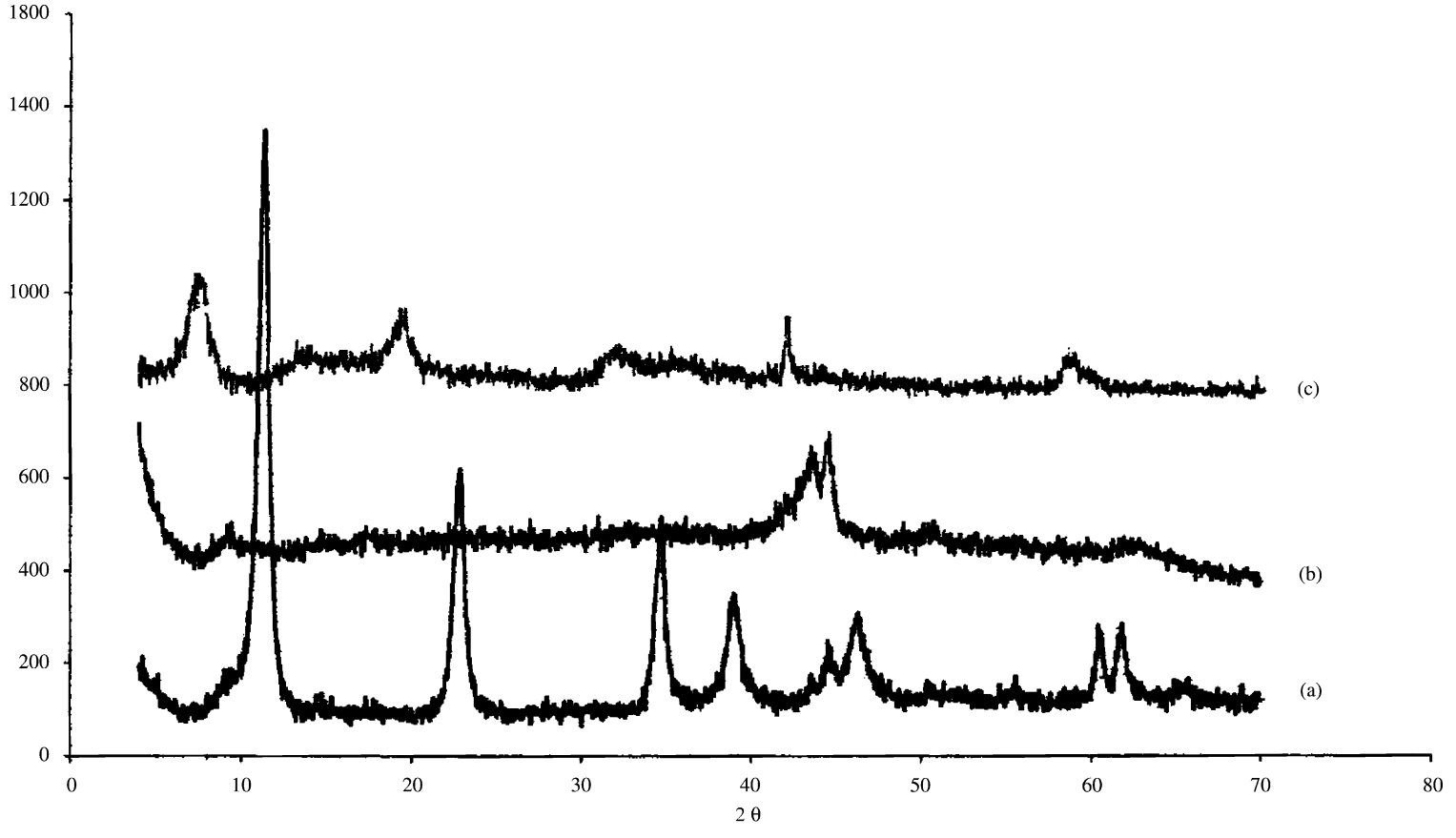

Fig. 1. XRD patterns of (a) Mg/Al LDH, (b) Mg(Al)O, and (c) Mg(Al)O after condensation and dehydration reactions.

Table 1
Physico-chemical properties of the catalysts and initial reaction rates in the condensation between propanal and benzaldehyde ([propanal]/[benzaldehyde] = 1.5) at 403 K

Sample	S_{BET} ($m^2\,g^{-1}$)	ΔH (CO_2) ($kJ\,mol^{-1}$)	N_B[a] ($mol\,g^{-1}$)	N_A[b] ($mol\,g^{-1}$)	N_B/N_A	$V_0 \times 10^6$ ($mol\,l^{-1}\,s^{-1}$) (propanol)	$V_0 \times 10^6$ ($mol\,l^{-1}\,s^{-1}$) (propanol/H_2O = 97/3)
NaCs-BEA	680	31	0.8	0.03	27	0	–
MgO	268	76	1.15	0.12	9.6	1.6	2.4
Mg(Al)O	230	66	1.62	0.19	8.5	3.9	7
Pd/Mg(Al)O	230	74	1.23	0.24	5	–	8[c]

[a] Number of basic sites.
[b] Number of acidic sites.
[c] [Propanal]/[benzaldehyde] = 4.

presents the higher N_B/N_A ratio between the number of basic and acidic sites accounting for a low amount of acidic sites after alkaline exchange. MgO exhibits the higher basic character with stronger basic sites than Mg(Al)O and Pd/Mg(Al)O, and lower amount of acidic sites. This is in agreement with the presence of strongly basic O^{2-} sites in MgO, and of Al^{3+}–O^{2-} acid–base pairs with probably also minor amounts of OH^- sites in Mg(Al)O. Remarkably the impregnation with Pd(acac) of Mg(Al)O decreases the number of basic sites with, in contrast, an improvement of the basic strength. Indeed formation of strong O^{2-} sites at the boundary of the metal particles was reported for Pd/Mg(Al)O [14]. It is noteworthy that Mg(Al)O and Pd/Mg(Al)O possess the higher amounts of acidic sites confirming the high amount of acid–base pairs in these samples. TPR and H_2 chemisorption experiments of Pd/Mg(Al)O show a total reduction of Pd at 473 K and a $(H/Pd)_{irr}$ ratio of 0.27.

3.2. Catalytic tests

A simplified reaction scheme shown in Fig. 2 can be proposed for the reaction of benzaldehyde and

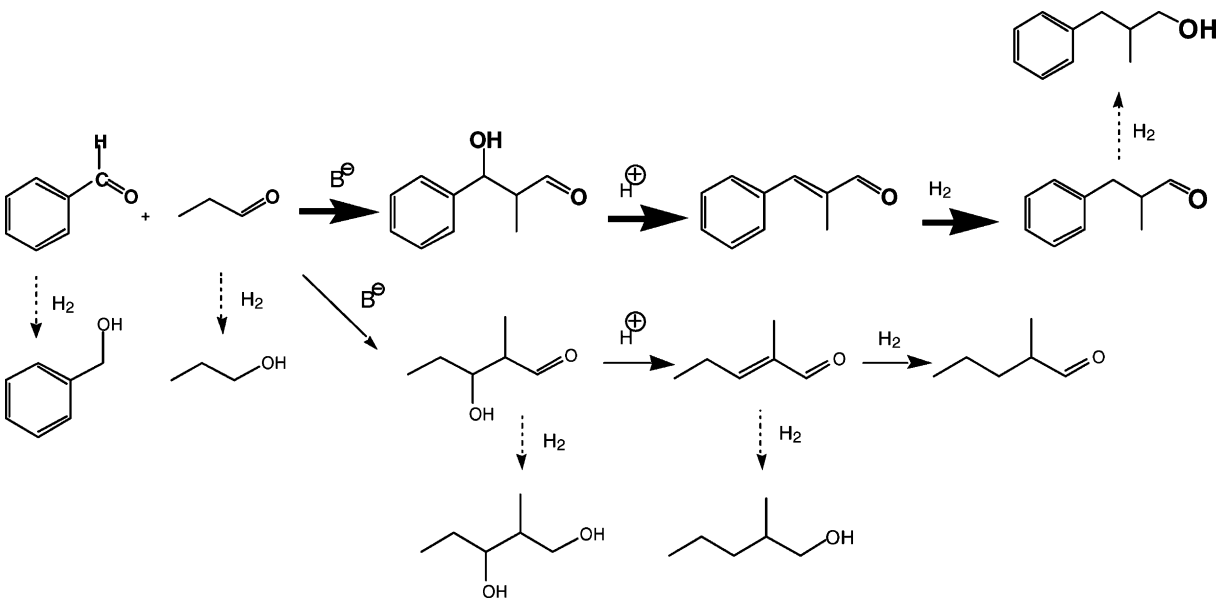

Fig. 2. Simplified scheme of the reaction between benzaldehyde and propanal with hydrogen on a solid catalyst containing basic, acidic and hydrogenating sites.

propanal with a catalyst exhibiting basic, acidic and hydrogenating sites. Selectivity toward 2-methyl-3-phenyl-propanal will depend on the balance between acido-basic and hydrogenating properties mainly controlled by the nature of the support and the Pd amount. A very high basic support will favor successive condensation reactions, while on the other hand deep hydrogenations towards alcohols will take place when the hydrogenating function dominates. The condensation reaction between benzaldehyde and propanal was first studied with the different solids at 403 K. The propanal/benzaldehyde molar ratio was 1.5 and propanol was used as solvent. Mg(Al)O leads to the higher initial reaction rate (Table 1) with a selectivity toward the α-methyl-cinnamaldehyde of 23% for a maximum conversion of 33% in benzaldehyde (actually some benzaldehyde and α-methyl-cinnamaldehyde remaining adsorbed within the pores could not be taken into account). Higher activity of Mg(Al)O as compared to MgO could be explained by the higher number of both basic and acidic sites in the former (Table 1). However, the vicinity of the acidic and basic sites giving rise to acid–base pairs characteristic of these mixed oxides could favor the consecutive reactions of condensation and dehydration. Noteworthy the acid–base pairs are the major species present on Mg(Al)O calcined at 623 K with minor amount of remaining OH also active for the condensation [15]. It is known that the catalytic activities of Mg(Al)O and MgO for the aldol and Knoevenagel condensation reactions are enhanced upon addition of H_2O in the reaction medium or by a careful rehydration of the mixed oxide leading to a reconstruction of the LDH [15,16]. Indeed OH^- basic sites thus formed are more active than O^{2-} sites to catalyze the aldol condensations. Therefore, the condensation between benzaldehyde and propanal has been performed in a propanol/H_2O mixture (3/97, w/w). The initial reaction rates are twice faster than in propanol (Table 1). Mg(Al)O remains the most active catalyst, moreover the selectivity toward the α-methyl-cinnamaldehyde increases to 66% for a conversion of 43%. Self-condensation of propanal into 2-methyl-penten-2-al lead to the main secondary product. It is noteworthy that the XRD pattern of this used catalyst is characteristic of the LDH structure (Fig. 1), showing that a reconstruction occurs during the catalytic reaction and that OH^- are the most active sites. The interlayer distance of 0.763 nm in the precursor increases to 1.20 nm after reconstruction due to the swelling by propanol. As expected NaCs-BEA is poorly active accounting for its low basicity.

The influences of two important reaction parameters: the nature of the solvent and the reactants ratio, have been examined using Mg(Al)O as catalyst. The reaction is totally inhibited in methanol; this slightly acidic molecule poisoning the stronger active basic sites of the catalyst. In ethanol hydride transfer reactions generate acetaldehyde and benzyl alcohol, leading to undesired products by condensation of acetaldehyde and benzaldehyde. Moreover, ethanol was a good solvent for aldol condensations in homogeneous conditions [17], and also gives the best conversion in the condensation of benzaldehyde and acetone [10]. Finally, propanol appears as the most appropriate solvent.

The dependence of the initial reaction rate (disappearance of benzaldehyde) upon the concentration of propanal, at constant concentration of benzaldehyde ($0.4\,mol\,l^{-1}$), is reported in Table 2. A maximum of reactivity is observed for a concentration of $1.6\,mol\,l^{-1}$. This behavior agrees well with Langmuir–Hinshelwood (L–H) kinetics of a bimolecular reaction. A simplified rate equation could be $V = k\lambda_b C_b \lambda_p C_p / (1 + \lambda_b C_b + \lambda_p C_p)^2$, where k is the rate constant, C_b and C_p the concentrations of benzaldehyde and propanal, and λ_b, λ_p are the adsorption coefficients of benzaldehyde and propanal, respectively. From the kinetic law it is well known that the concentration at the maximum is related to λ_b/λ_p, the ratio of the adsorption coefficients [18]. The rate goes through a maximum at C_p/C_b of 4. We have indeed an L–H competitive mechanism with benzaldehyde strongly adsorbed than propanal (Table 2). This induces that the higher conversion and selectivity for the cross-condensation product is obtained with propanal in excess. As expected the selectivity towards α-methyl-cinnamaldehyde decreases at low reactant ratio due both to the high benzaldehyde adsorption and the low propanal concentration. At high ratio it decreases because self-condensation of propanal into 2-methyl-penten-2-al becomes the main reaction.

Mg(Al)O exhibiting the more interesting catalytic properties for the condensation, it was used as support for Pd. An amount of 0.2 wt.% Pd was deposited based on our previous results showing that the highest

Table 2
Results for the condensation reaction between benzaldehyde and propanal at different [propanal]/[benzaldehyde] molar ratios

[Propanal]/[benzaldehyde]	$V_0 \times 10^6$ (mol l^{-1} s^{-1})	Conversion (%)		Selectivity of 2-methyl-3-phenyl-propanal (%)
		Benzaldehyde	Propanal	
1.5	7.0	43	100	66
4	10.4	44	96	97
10	5.8	32	83	77

selectivity to MIBK in the condensation of acetone was achieved at this amount [6]. The reaction between benzaldehyde and propanal performed at 403 K under 1 MPa H_2 pressure in propanol/H_2O as solvent lead to 43% conversion with a selectivity of 45% of 2-methyl-3-phenyl-propanal. Secondary products arise from α-methyl-cinnamaldehyde (8% selectivity), 2-methyl-penten-2-al and 2-methyl-penten-2-ol, traces of benzyl alcohol and 2-methyl-3-phenyl-propan-1-ol. Selectivity to the target molecule could probably be improved, avoiding the self-condensation of propanal, by a stoichiometric addition of propanal on benzaldehyde.

4. Conclusions

A multifunctional Pd/Mg(Al)O catalyst (0.2 wt.% Pd) obtained from hydrotalcite precursor is an active catalyst to perform with good yields the "one-pot" synthesis of 2-methyl-3-phenyl-propanal from benzaldehyde and propanal. The addition of H_2O to the solvent improves the catalytic activity of the support for the condensation by enhancement of the Brønsted basic character. The synthesis in "one-pot" of other high molecular weight ketones or aldehydes, particularly those involving substituted benzaldehydes or long chains aliphatic ketones is a challenging objective which is in progress.

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