Catalysis Today 167 (2011) 71–76

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Hydrotalcite-derived mixed oxides as catalysts for different C–C bond formation reactions from bioorganic materials

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ARTICLE INFO

Article history:
Received 19 May 2010
Received in revised form 3 November 2010
Accepted 5 November 2010
Available online 18 December 2010

Keywords:
Aldol-condensation
Biomass conversion
Biofuels
Basic catalysis
Bioethanol upgrading
Ketone upgrading

ABSTRACT

The performance of a hydrotalcite-derived mixed oxide (Mg_3AlO_x) for the three different aldolization reactions, concerned with the valorisation of biomass derivatives, has been studied in this work. The studied reactions were acetone self-condensation, ethanol condensation for the synthesis of C_4 chemicals, and the aldolization of aqueous mixtures of acetone and furfural. The gas phase condensation of acetone generates mesityl oxide (C_6) and isophorones (C_9) as main products, with high selectivities for mesityl oxide (up to 80%). Reaction of ethanol leads to butanol and 1,3-butadiene, although important amounts of undesired ethylene were found at the highest temperatures. Concerning to the liquid-phase condensation of furfural with acetone, C_8 and C_{13} species were found as reaction products. The performance of the catalysts can be explained in terms of the distribution of acid and basic sites determined by NH_3- and CO_2-TPD, being needed medium strength basic sites (M^{n+}–O^{2-} pairs) for the condensation reactions, whereas the presence of acid–base pairs are needed for alcohols dehydrogenation (previous step for the condensation when ethanol is used as reactant). The presence of acid sites also leads to lateral reactions, such as the dehydration of ethanol or the rearrangement of lineal phorones into cyclic compounds (isophorones) in the reaction of acetone.

1. Introduction

The use of biomass as raw material for the synthesis of fuels and chemicals is nowadays a major challenge because of the scarcity of fossil fuels and the global climate change concerns. Although from a thermodynamic point of view, the use of biomass for satisfying the needs of fuels and chemicals is reliable [1], many technological limitations burden this possibility. Only a very minor fraction of this biomass (triglycerides, sugars and starches) can be selectively transformed into fuels (biodiesel) or chemicals (mainly ethanol), whereas most of the biomass components (cellulose, lignin) are not easy to transform into valuable organic molecules. Most of the treatments of the whole biomass (such as pyrolysis or acid/enzymatic hydrolysis) lead to the formation of low-rank organic molecules of low molecular weight and high oxygen/carbon ratio. In this way, bioethanol is obtained in the fermentation of sugars and starches; chemicals such as acetone, acetic acid, phenols, furfural and other light oxygenates are released during the fast pyrolysis of biomass feedstock [2], and large amount of oxidised derivatives of the sugars (such as furfural, hydroxymethylfurfural, glucuronic acid) are formed during the acid hydrolysis of wooden feedstocks [3].

The transformation of molecules of low molecular weight into larger molecules must involve the formation of new carbon–carbon bonds. Aldol-condensation reactions, taking place between two molecules with carbonyl groups (aldehydes or ketones), allow the formation of these bonds at mild conditions, but needing a basic catalyst. The mechanism of base-catalysed reaction involves equilibrium formation of the enolate ion, following by the addition of the enolate to the carbonyl group of the second aldehyde or ketone. Depending on the base concentration and the operation temperature, successive elimination steps are also possible, leading to unsaturated carbonylic compounds [4]. A subsequent reaction of these adducts lead to alcohols or olefins, of higher molecular weight than the parent molecule. The basic material also catalyses the transformation of alcohols into carbonylic compounds (aldehydes for primary alcohols and ketones for secondary alcohols), allowing the use of alcohols as raw materials for this kind of reactions (known as Guebert reactions when alcohols are used as reactants [5]). The liquid-phase condensation of furfural and acetone, proposed by Dumesic and co-workers [6,7] as the initial step in the preparation of diesel fuels; the preparation of C_4 chemicals (butenes, budiene, butanol, etc.) from bioethanol [8,9], and the formation of C_6 and C_9 chemicals (including alcohols and aromatic compounds such as mesytilene) from acetone [10,11], are typical

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doi:10.1016/j.cattod.2010.11.056

applications of this kind of reactions in the field of the valorisation of biomass derivatives.

Different basic catalysts have been proposed for these reactions, such as MgO (proposed by Ndou et al. [12] for ethanol dimerization), hydroxyapatite (proposed by Tsuchida et al. [8] for the same reaction), magnesia–zirconia mixed oxides (proposed by Barret et al. [7] for aldol condensation of acetone and furfural in liquid phase), or niobium oxides (proposed by Paulis et al. [13] for acetone self-condensation). Among these materials, Mg–Al mixed oxides derived from hydrotalcite precursors are very interesting catalysts since they are relatively cheap, does not contain toxic metals, and present enhanced stability both at high temperatures and in aqueous solutions [14]. In a previous work [15], we have shown that the alkaline properties of these materials are strongly dependent on chemical composition and synthesis procedure. On the other hand, the presence of both acid and basic sites, the nature of basic sites, its density, or the presence of an external solvent, largely affects its performance in condensation reactions, since these reactions involve a complex sequence of elemental steps catalysed either by basic or acid sites, as well as by combinations of these sites.

The scope of the present work is the study of three different condensation reactions of practical interest (liquid-phase condensation of acetone and furfural, gas-phase ethanol dimerization and gas-phase acetone self-condensation) over hydrotalcite-derived mixed oxides. Acetone, often obtained by thermochemical treatment of biomass, can form via aldol condensation dimmers of acetone (such as mesityl oxide) or cyclic compounds (such as mesytilene). Ethanol is obtained from the fermentation of carbohydrates, and can be used directly as fuel or as raw material of derivates. Aldol condensation of ethanol yields C_4 compounds such as 1-butanol (additive to gasoline or solvent) [12] or 1,3-butadiene (used in the polymerization of synthetic rubber. Furfural is obtained from cellulose after an aqueous-phase process, such as acid hydrolysis. Its condensation with acetone produces large organic compounds, which after dehydration/hydrogenation are converted into a paraffinic mixture equivalent to biodiesel [6]. All these compounds are interesting raw materials in organic chemical industry.

2. Experimental procedure

2.1. Catalysts preparation

Mg–Al layered double hydroxide (LDH) with Mg/Al ratio of 3 was synthesized by coprecipitation at low supersaturation conditions (constant pH), according to the previously reported procedure [15]. The material was prepared mixing 1 M solutions of $Mg(NO_3)_2 \cdot 6H_2O$ (Fluka, >99%) and $Al(NO_3)_3 \cdot 9H_2O$ (Panreac, 98%) in 3/1 molar ratio. A volume of 150 mL of this solution was added drop wise to 100 mL of K_2CO_3 (Panreac, 99%) 0.2 M under sonication at 298 K. The pH was kept at 10 by adding appropriate quantities of 1.6 M NaOH (Prolabo, 98%) solution. After that, the precipitate was separated by high-speed centrifugation, washed in deionized water in order to remove the alkali metals and the nitrate ions until pH 7, and dried in oven at 373 K for 24 h. The resulting hydrotalcites were calcined in air flow at 723 K for 7 h to obtain the mixed oxides.

2.2. Reaction studies

Three different reaction studies were carried out: aldolization of acetone (reaction (1)), aldolization of ethanol (reaction (2)) and aldol condensation of furfural with acetone (reaction (3)). For reactions (1) and (2), a fixed bed reactor consisted of a 0.4 cm i.d. U-shaped quartz placed in electric furnace controlled by PID was employed. The catalyst (about 150 mg) was placed over a plug of quartz wool and a thermocouple was placed inside the catalyst bed. A helium flow of 0.05 L min^{-1} (s.t.p.) of acetone (3.2 vol.%) or ethanol (5.5 vol.%) – both supplied by Panreac, 99.5% – was fed. Outgoing gases from the ethanol reaction were analyzed on-line using by mass spectrometry after chromatographic separation (Shimadzu QP-2010). The spectrometer was previously calibrated for reaction product response. Conversion was calculated based on peak areas of ethanol. For acetone reaction, products were collected in a cold trap (mixture of liquid nitrogen and isopropanol) and analyzed by gas chromatography. Product identification was confirmed by analysis in a GC–MS (Shimadzu QP-2010), using the same column and conditions that in the gas chromatograph. Mass balance closures were always higher than 90%.

For the reaction (3), experiments were carried out in a 0.5 L stirred batch autoclave reactor (Autoclave Engineers EZE Seal, 500 mL) equipped with a PID temperature controller and a back pressure regulator. The reactor was loaded with 0.25 L of an aqueous solution of furfural (Panreac, 98%) and the catalyst (500 mg, with an average particle diameter of 50–80 μm), and air was purged out by adding nitrogen up to 55 bar for three times before starting the condensation reaction. Acetone (Panreac, 99.5%) was introduced to start the reaction, resulting a 5% of organic compounds in aqueous solution (furfural: acetone molar ratio of 1:1). Then, the reactor was pressurized to 10 bar with N_2, heated to reaction temperature, and stirred at 1000 rpm for 24 h. Samples (12–15 samples of 1 mL) were withdrawn from the sampling port during the condensation reaction. Samples were filtered, extracted in ethyl acetate and automatically analyzed by capillary GC in a Shimadzu GC-2010 apparatus equipped with a FID detector, using a 15 m long CP-Sil 5 CB capillary column as stationary phase. Peak assignment was performed by GC–mass spectra and responses were determined using standard calibration mixtures.

2.3. Catalysts characterization

The crystallographic structure of the mixed oxide was determined by XRD using a Philips PW 1710 diffractometer, working with the Cu-K$_\alpha$ line (λ = 0.154 nm) in the range 2θ between 5° and 85° at a scanning rate of 2θ of 2°/min. Textural characteristics of specific surface area and pore volume were estimated by nitrogen adsorption at 77 K in a Micromeritics ASAP 2020 surface area and porosity analyzer. The strength and distribution of the basic sites were determined by temperature programmed desorption of preadsorbed CO_2 in a Micromeritics TPD/TPR 2900 apparatus. Samples (10 mg) were treated in He at 723 K for 0.3 h and exposed to a CO_2 stream at 323 K temperature until saturation coverage were reached. Weakly adsorbed CO_2 was removed by flushing with He at the same temperature for about 0.3 h. The temperature was then increased at a linear rate of 5 K/min from 293 to 723 K and the rate of CO_2 evolution was monitored by mass spectrometry. The same apparatus was used for NH_3-TPD. In this case, the sample was firstly cleaned at 723 K, then cooled to 323 K and saturated with NH_3 (5% in helium) for 0.3 h. Then, samples were purged for 0.3 h in He before starting the TPD experiments under He from 323 to 723 K.

3. Results and discussion

3.1. Characterization of catalyst

The catalyst used in this work has been selected from a systematic comparison of hydrotalcite-derived materials prepared by different methods and under different reaction conditions [15]. The selected magnesium–aluminium double oxide presents a high CO_2 adsorption capacity (measured by thermogravimetry at 0.1 MPa and 323–373 K), a low percentage of CO_2 irreversibly adsorbed, and

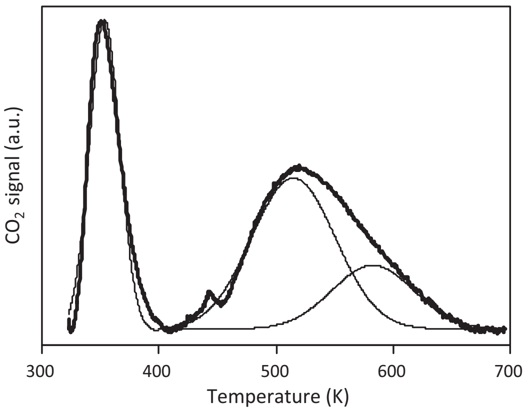


Fig. 1. CO_2-TPD profile of the Mg_3AlO_x. Thin lines corresponding to the deconvolution of the profile.

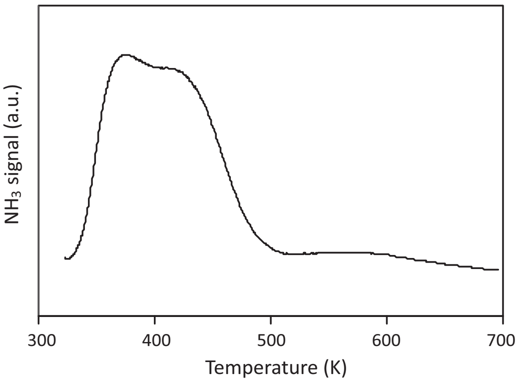


Fig. 2. NH_3-TPD profile of the Mg_3AlO_x.

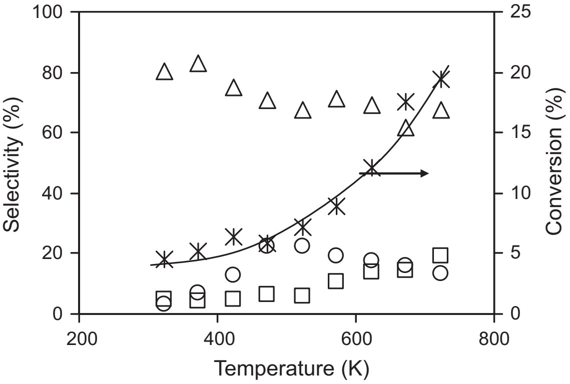


Fig. 3. Influence of the reaction temperature on the conversion (*) and selectivities towards the main reaction products in the condensation of acetone: diacetone alcohol (□), mesityl oxide (△) and α-isophorone (○).

a similar ratio of the strongest basic sites (monodentate carbonates) and the weakest sites (bidentate carbonates and bicarbonates) – determined from the highest vibration modes of the FT-IR spectra.

Elemental analysis of the catalyst gave an Mg/Al ratio of 3, very similar to the precursor solution. Thermal decomposition of the hydrotalcite precursor led to the formation of a mixed oxide with a surface area of 142 $m^2\,g^{-1}$ and significant porosity (0.82 $cm^3\,g^{-1}$). Diffraction pattern is consistent with the presence of a crystalline MgO periclase phase (JCPDS 45-946), whereas aluminium compounds are either well-dispersed or in amorphous phases. A quantitative measurement of the basic site strength was obtained by CO_2-TPD, Fig. 1. This profile showed three desorption peaks at 353 K (59 μmol g^{-1}), 518 K (79 μmol g^{-1}) and 580 K (33 μmol g^{-1}).

From IR measurements reported in our previous work [15], it was observed that after CO_2 adsorption at 298 K, bicarbonates, as well as unidentate, chelating bidentate and bridged bidentate carbonates were formed. Bicarbonates and bridging bidentate carbonates disappear above 373 K, chelating bidentate carbonates above 473 K, and a fraction of unidentate carbonates remain after evacuation at 673 K [15]. Hence, in TPD experiment, the low temperature desorption peak corresponds to bicarbonate (species adsorb on weakly basic OH groups) and bridging bidentate carbonate (bidentate carbonates adsorb on Mg–O site pairs, bridging carbonates require two cationic sites). The medium temperature peak could be attributed to chelating bidentate carbonates (species formed on just one Mg^{2+} site), and the high temperature TPD desorption peak would correspond to unidentate carbonated, species formed on strongly basic surface O^{2-} anions.

The NH_3-TPD profile of the calcined hydrotalcite is shown in Fig. 2. Ammonia desorption starts at about 330 K, reaching a first maximum at 380 K, and a shoulder centred at about 420 K, with a total ammonia release of 129 μmol g^{-1}. The first peak is associated to physisorbed and very weakly adsorbed ammonia, corresponding to the weakest Bronsted acid sites, whereas the second one is attributed to NH_3 adsorbed on strong Lewis acid sites [16,17]. These authors also found that Mg–Al mixed oxides present mainly Lewis acidity. In summary, the catalyst here tested presents similar characteristics (both amount of acid and basic sites, and its distribution) to mixed oxides used for base-catalysed reactions [9,18–20].

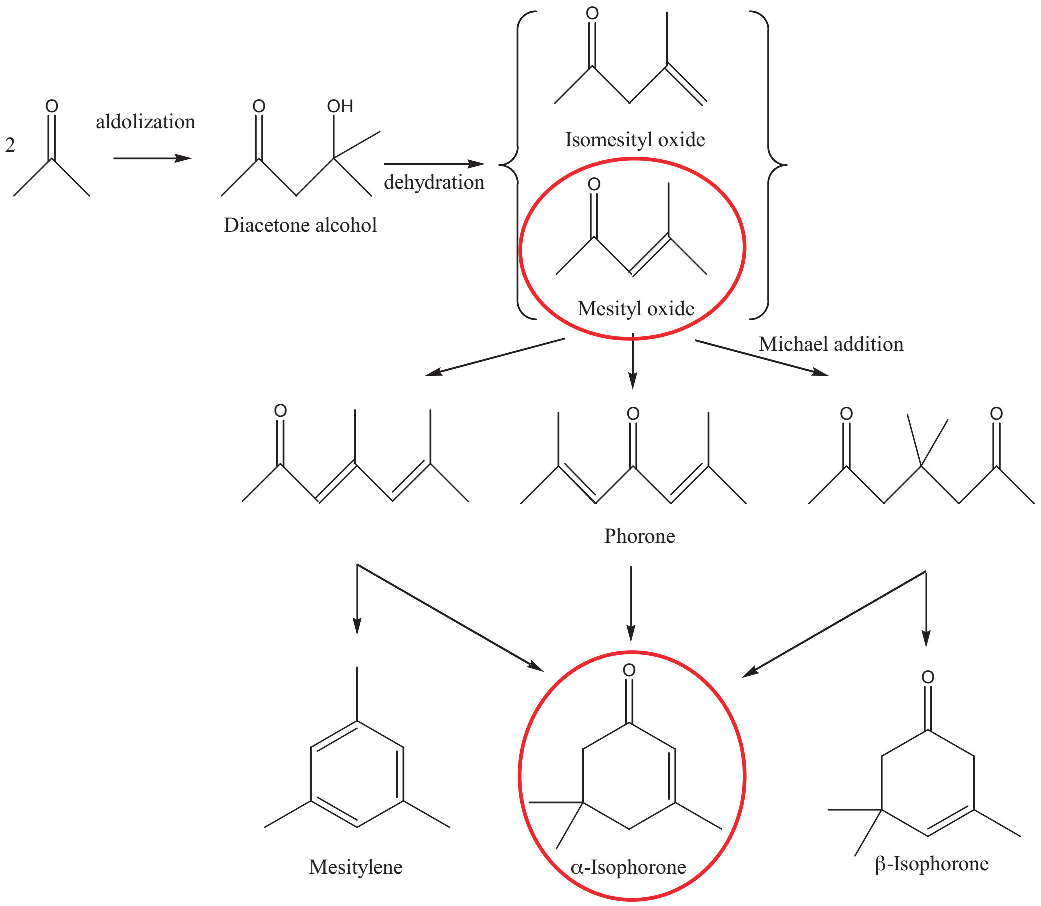
3.2. Gas-phase acetone self-condensation

Gas phase condensation of acetone was performed over the Mg_3AlO_x catalyst at temperatures between 323 and 723 K. Additionally, a blank experiment was carried out at 723 K using a bed of quartz instead of the catalyst, without observing any reaction product. Overall conversion and selectivity to the main reaction products – diacetone alcohol (C_6), mesityl oxide (C_6) and α-isophorone (C_9) – are summarized in Fig. 3. Other minor products detected were: isomesityl oxide (C_6), phorone (C_9), mesitylene (C_9) and β-isophorone (C_9), Table 1.

According to the results obtained and the reaction pathways suggested in the literature [13,19], the mechanism summarized in

Table 1
Summary of the catalytic results (conversion and selectivity) for the gas phase aldol condensation of acetone over Mg_3AlO_x (150 mg catalyst, 3.2% acetone in He flow).

Temperature (K)	323	423	523	623	723
Conversion (%)	4.5	6.3	7.3	12	19
Selectivity (%)					
Diacetone alcohol	4.9	4.7	6.0	13.9	19.1
Isomesityl oxide	0	0	0.08	0.3	1.7
Mesityl oxide	80.0	74.9	68.6	69.1	67.8
Phorone	3.1	3.9	1.6	1.4	0.5
Mesitylene	2.1	1.0	0.6	3.1	3.2
α-Isophorone	3.1	12.6	22.6	17.6	13.3
β-Isophorone	2.5	1.7	1.5	0.3	0.6



Scheme 1. Reaction scheme of gas phase aldol condensation of acetone. In circles the major reaction products.

Scheme 1 is proposed for this reaction. According to this scheme, aldol condensation of acetone leads to diacetone alcohol, which selectively increases with the temperature, especially above 600 K. Aldolization requires base catalysis. More concretely, this step involves acid–base pair sites [9]; thus the surface Mg^{2+}–O^{2-} pairs, medium strength base sites, are involved in this condensation [15]. Diacetone alcohol decomposes by dehydration into either mesityl oxide or isomesityl oxide. Mesityl oxide is the major product in this reaction (70–80%), whereas the isomesityl oxide hardly gets 1% of selectivity (Table 1). The high selectivity towards the first isomer is a consequence of the basic character of the catalyst [13]. According to this mechanism proposed, a Michael addition of acetone leads to different linear trimers, phorone, and so on tetramers or pentamers. Nevertheless, phorone was always observed in very small amounts (Table 1), thereby suggesting that the compound rearranges rapidly to yield cyclic products. α-Isophorone is the major C_9 product, and its formation requires the presence of stronger basic sites than the C_6 products [20]. The O^{2-} basic sites could be responsible of this rearrangement. Selectivities for mesitylene and β-isophorone are very low, about 3 and 2%, respectively. This is in agreement with the basic character of the catalyst, since the formation of these cyclic compounds is catalysed by medium-acidity sites [13]. These authors also report the decomposition of trimers, tetramers and pentamers into acetic acid, compound not detected in our experiments. It should be also pointed out that neither isopropanol nor methyl isobutyl ketone (compounds reported in the self-condensation of acetone [18]) are detected. Both kinds of reactions are catalysed with active phases with redox properties, which are not present in the studied material. Product distribution here reported for the condensation of acetone is congruent with data reported in the literature for this reaction on mixed oxides with similar distribution of basic sites; however, if the reaction is carried out on a more acidic catalyst, the selectivity towards mesitylene could get values of 50% [18].

3.3. *Aldol condensation of ethanol (Guerbet reaction)*

The reactivity of ethanol was tested at similar conditions, a blank experiment was also carried out at the maximum reaction temperature, negligible conversion being obtained. Results of conversion and selectivities for C_2 and C_4 products are summarized in Fig. 4.

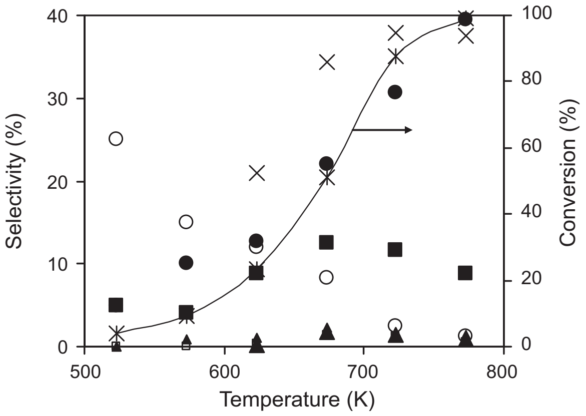
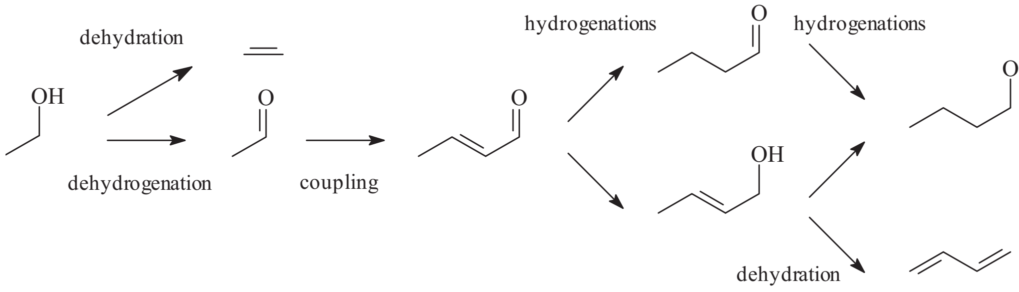


Fig. 4. Influence of the reaction temperature on the conversion (*) and selectivities towards the main reaction products in the ethanol condensation: acetaldehyde (●), ethylene (×), 1-butanol (○), 2-butenal (♦), 2-buten-1-ol (□), butanal (▲), and 1,3-butadiene (■).



Scheme 2. Mechanism for ethanol condensation.

It is observed that the selectivity for acetaldehyde and ethylene increases as temperature increases, whereas the selectivity for C_4 products trends to decrease with increasing temperatures. In addition, some other heavier products (n-C_6, n-C_8, and n-C_{10} alcohols and olefin derivatives) were formed by subsequent condensation, being the selectivities for the formation of these compounds lower than 10%. Results obtained are, in terms of the selectivities obtained for C_4 fraction, better than the obtained with MgO catalysts tested at similar conditions [12], and slightly worse than the obtained with an optimised formulation of a hydroxyapatite catalysts [8].

In general terms, selectivities for condensation products are lower than in the case of acetone. The complexity of the reaction pathways, involving elementary steps not leading to condensation products (for example dehydration yielding ethylene) justifies this behaviour. On the other hand, additional dehydrogenation steps for transforming alcohols into aldehydes are also required for obtaining condensation products. Although this last reaction is also catalysed by basic sites, the chemical requirements of these sites are different in both reactions (dehydrogenations and condensations).

According to the results obtained and the reaction pathways proposed in the literature [8,9], the mechanism summarized in Scheme 2 is proposed for this reaction. Acetaldehyde is obtained from ethanol by dehydrogenation. This reaction involves the dissociative adsorption of ethanol on acid–base pairs [21]. The surface M^{n+}–O^{2-} pairs, sites on which chelating and bridging bidentate carbonates are formed [15], catalyse this reaction since cationic sites adjacent to oxygen positions are required. Condensation of adsorbed acetaldehyde molecules to form n-butanol requires the formation of a carbanion intermediate. This step involves both acid–base pair sites, but also a high density of basic sites [9]. Thus, the higher concentration of the surface M^{n+}–O^{2-} pairs, the higher extent of this reaction. 2-Butenal, 2-buten-1-ol, and butanal are formed as intermediate species that finally hydrogenate to 1-butanol [12], justifying their low selectivity in the reaction. These hydrogenation reactions have been found by other authors, suggesting that they are caused by the recombination of the organic molecules with hydrogen atoms resulting from the alcohol dissociative adsorption [9]. 2-Butenal and 2-buten-1-ol are also intermediates in the formation of 1,3-butadiene by the Lebedev reaction [8]. According to this reaction, that requires acid and basic sites, acetaldehyde is both reactive and catalyst, thus a decrease in acetaldehyde yield is observed at the beginning of 1,3-butadiene production. Finally, ethylene is the result of the ethanol dehydration, which requires the presence of acid sites [9]. These authors reported the benefits for ethylene formation of the presence of high density of $Al^{3+}O^{2-}$ pairs and lower density of strong basic sites. Thus, the Lewis acidity observed from the NH_3-TPD could be responsible of the ethylene formation. It is remarkable that the experiments carried out at the lowest temperature, do not yield to the formation of dehydration products (negligible selectivities for ethylene formation), being the formation of these products largely increased as temperature increases. This result suggests that there is a temperature interval at which the basic sites are active, but the acid sites are not active for dehydration reactions. More detailed studies, varying the strength and concentration of acid and basic sites also support these assumptions [22].

Results shown here are in agreement with data reported in the literature for similar catalysts [9]. Materials with the strongest basic sites (e.g. MgO) presents low activity, since the O^{2-} groups hinder the ethanol dissociative adsorption; whereas samples with higher amounts of acidic groups (hydrotalcites derived mixed oxides with low Mg/Al ratio) favour the dehydration reaction towards ethylene [9].

3.4. *Aldol condensation of furfural with acetone*

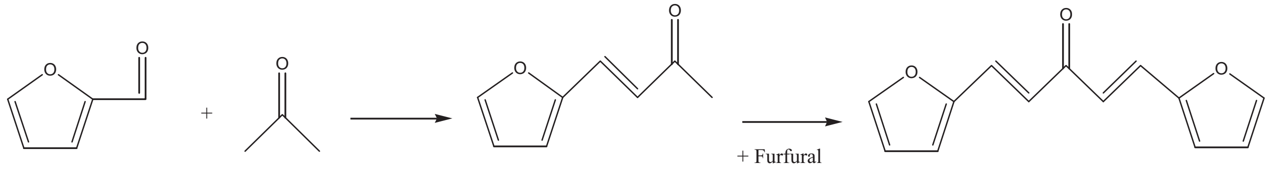
Liquid phase condensation of furfural with acetone was performed over the Mg_3AlO_x catalyst at temperatures between 323 and 373 K. As in previews reactions, a blank experiment was carried out without catalyst, in which no products were observed. Condensation of furfural with acetone forms C_8 and C_{13} compounds, Table 2. These C_8 and C_{13} species are considered as the precursors of diesel-quality biofuels after a deep hydrogenation reaction [6,7]. The analysis of the dimmers and trimers formed was carried out after liquid extraction in ethyl acetate.

Table 2 shows the experimental results obtained in the reaction of furfural with acetone at molar ratio 1:1, at reaction temperatures from 323 to 373 K and for different reaction times (batch reactor). The rate of furfural conversion of the reaction increases with the temperature; however, after 24 h of reaction, a ~70% of conversion is obtained. Although a more detailed kinetic study is needed for explaining reaction mechanism, the temperature independence of final conversion suggests complex reaction mechanism involving adsorbed species. Selectivity towards both C_8 and C_{13} increases

Table 2
Effect of temperature and reaction time on the product distribution of the aldol condensation of furfural with acetone (5 wt.% organic in aqueous phase, total volume: 250 mL, 0.5 g of catalyst).

	323 K			343 K			373 K		
Reaction time (h)	1	8	24	1	8	24	1	8	24
Carbon balance (%)	54.9	79.0	68.5	80.9	73.4	74.6	78.1	81.2	72.7
C_5 conversion (%)	10.4	33.7	69.9	40.5	54.0	68.0	46.4	48.8	65.5
C_8 selectivity (%)[a]	9.8	23.3	26.8	7.5	19.9	22.9	12.3	15.3	19.8
C_{13} selectivity (%)[a]	0.6	10.4	10.5	9.2	9.0	18.2	11.4	13.2	13.9

[a] Selectivity is calculated by mol of C_5.



Scheme 3. Reaction pathway for aldol-condensation of furfural with acetone.

with the time, being more notorious the effect of time in the heavier compound. The selectivity for the C_8 fraction decreases as temperature increases, suggesting a serial reaction pathway yielding C_{13} compounds. The only exception to this behaviour is the observed at the highest temperature and reaction time, a decrease on C_{13} selectivity being observed at this condition. This fact, as well as the low carbon balance closure found, suggests the presence of side condensation reactions leading to heavier products.

Scheme 2 summarizes the different steps for the ethanol condensation reaction. This aldol-condensation reaction begins with the abstraction of α-hydrogen from the acetone to form an intermediate carbanion, which then attacks the carbonyl carbon atom of furfural to form a C–C bond leading to a C_8 product (Scheme 3). Further condensation of the C_8 product with furfural forms a C_{13} compound. Thus, by analogy with the previous condensation reactions, both acid–base pair sites and high density of strong basic sites are required. Furthermore, the mixed oxide tested in this work also presents weak hydroxyl basic groups, being accepted that these sites are also active for liquid phase aldol condensations [20].

If our results are compared to the previously reported on $MgO–ZrO_2$ catalyst [6], it is observed that the C_{13} selectivity here reported is markedly lower, although obtained conversions are very similar. No clear conclusion could be obtained, since although the material here tested presents a higher amount of basic groups (171 μmol/g vs. 103 μmol/g), no quantitative information about the distribution of basic sites is available for the Mg–Zr mixed oxide. However, it must be taken into account that XPS analyses done for similar materials demonstrate the presence of both carbonates and bicarbonates [23].

4. Conclusions

Aldolization of organic molecules to increase the molecular weight of the resulting compound is a powerful tool in the valorisation of biomass derived molecules. Three reactions have been tested over a hydrotalcite derived mixed oxide (Mg_3AlO_x): self condensation of acetone and aldolization of ethanol, in gas phase; and aldolization of furfural with acetone, in liquid phase. The characterization of the surface chemistry using CO_2 and NH_3-TPD reveals the presence of basic sites of different strengths, as well as the presence of significant amounts of acid sites. In general, this material seems to provide good performance for reactions involving compounds with carbonyl groups, whereas their performance is not so good for alcohols, since the acidic groups promote the competitive dehydration of the alcohol yielding olefins. However, the activity of both types of sites seems to be tuneable by changing reaction temperature.

The basic-sites distribution of the studied materials also seems to favour the condensation of small molecules in comparison to the condensation of secondary condensation products, being observed high selectivities in the dimerization of acetone (which is positive from the point of view of the technological application of the reaction), as well as the formation of the C_8 fraction in the reaction of furfural and acetone (in this case, the C_{13} fraction is the most appreciated).

Acknowledgements

M. Ascariz is acknowledged for his help in the products identification by GC–MS. This work was financed by the Spanish Ministry for Innovation (contract MICINN-08-CTQ2008-06839-C03-02). M.L. and L.F. acknowledge their doctoral fellowship to the “Severo Ochoa” program of the Principality of Asturias (Spain).

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