Catalysis Today 223 (2014) 138–147

Contents lists available at ScienceDirect

Catalysis Today

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

Aldol condensation of furfural and acetone over Mg—Al layered double hydroxides and mixed oxides

Lukáš Hora[a,*], Vendula Kelbichová[a], Oleg Kikhtyanin[a], Oleg Bortnovskiy[b], David Kubička[a]

[a] Research Institute of Inorganic Chemistry, UniCRE-RENTECH, Areál Chempark Záluží, 436 70 Litvínov, Czech Republic
[b] Eurosupport Manufacturing Czechia, Areál Chempark Záluží, 436 70 Litvínov, Czech Republic

ARTICLE INFO

Article history:
Received 7 February 2013
Received in revised form 26 August 2013
Accepted 5 September 2013
Available online 14 October 2013

Keywords:
Aldol condensation
Hydrotalcites
Mixed oxides
Furfural
Renewables

ABSTRACT

Liquid phase aldol condensation of furfural and acetone catalyzed by solid base catalysts (Mg—Al hydrotalcites and Mg—Al mixed oxides) has been investigated as a method to valorize short chain ketones obtainable from biomass pyrolysis for the production of higher-molecular-weight products usable as fuel components. The Mg/Al molar ratios of the investigated catalysts was varied in the range from 2 to 4 and their catalytic activity was tested at different reaction temperatures (20–100 °C) using several activation methods. Mg—Al hydrotalcites were used either after calcination as mixed oxides or after subsequent contact with liquid water or steam as rehydrated materials.

Both furfural-acetone condensation products, i.e. C_8 and C_{13}, were the desired products of aldol condensation reaction. Higher reaction temperature facilitated the dehydration step and enhanced the catalyst selectivity to both dehydrated products (C_8 and C_{13}). The best results were achieved with calcined catalyst sample having Mg/Al molar ratio equal to 3 at 100 °C (>95% furfural conversion and >90% selectivity to the desired products). The selectivity to the main by-product, diacetone alcohol, did not exceed 5% in any experiment. The ex situ rehydration of the calcined samples resulted in catalysts with a significantly lower activity, except the catalyst with Mg/Al molar ratio equal to 2. On the other hand, in situ rehydration caused catalyst activity improvement only in the case of the sample with Mg/Al molar ratio 3.

1. Introduction

The extensive use of fossil fuels has been a cornerstone of the rapid development during twentieth century, but it has also resulted in many adverse environmental impacts. Consequently, enormous research focus has recently been directed toward the sustainable utilization of renewable resources in an attempt to replace at least partially the finite fossil fuels resources [1,2]. The primary objective of these efforts is to maximize the sustainable utilization of biomass-derived feedstocks while minimizing environmental impacts (CO_2 emissions, loss of diversity, etc.) and avoiding competition with food and fodder production. It is particularly desirable to produce liquids fungible with conventional fuels and chemicals production from non-food crops [3–5].

A promising route to using the chemical potential of cellulose-rich feedstocks is their hydrolysis yielding furfural or hydroxymethylfurfural that are often denoted as platform chemicals [6–8]. For example, furfural can be obtained by acid hydrolysis of sugar cane bagasse, a residue from sugar cane processing, followed by extraction [9]. To exploit the full potential of furfural as a platform chemical its transformation by aldol condensation with acetone followed by hydrogenation/deoxygenation has been proposed to afford hydrocarbons, namely C_8 and C_{13} alkanes [10].

Typically, aldol condensation is catalyzed by homogenous base catalysts, such as sodium and calcium hydroxide. However, these processes generate significant waste water streams that must be treated (neutralized and cleaned) [10]. Apart from the negative environmental impact, the production cost is affected adversely. Consequently, many researchers focus on developing a new active and stable solid base catalyst (such as MgO [11], MgO—ZrO [10,12], ZnO, TiO_2 [13]) to replace the generally used homogenous catalysts [14,15]. Among the solid base catalysts, layered double hydroxides (LDH) also known as anionic clays or hydrotalcite like materials (HTC) have been also reported to be promising aldolization catalysts [16–19]. The main advantages of heterogeneous catalysts over homogeneous ones include easier catalyst recovery and recycling resulting in mitigation of the adverse environmental impacts, such as waste water treatment, and elimination of corrosion problems to name the most significant ones.

---

* Corresponding author.
E-mail address: lukas.hora@vuanch.cz (L. Hora).

0920-5861/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cattod.2013.09.022

The name “hydrotalcites” is reserved for solids having structure closely related to that of the mineral hydrotalcite, that is, rhombohedral $Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$. Hydrotalcites consist of a brucite-like $[Mg(OH)_2]$ network wherein isomorphous substitution of Mg^{2+} ion by a trivalent cation M^{3+} occurs and the excess positive charge is compensated by gallery anions which are located in the interlayer along with water molecules [20–22]. The Mg—Al LDH can be used as catalysts either in the form of mixed oxides Mg(Al)O obtained by the calcination of an Mg—Al hydrotalcite precursor or in the rehydrated form of these calcined materials [23].

The aim of this work is to describe the effect of pretreatment of the hydrotalcite-based catalysts on their activity and selectivity in aldol condensation of furfural with acetone. Besides calcination of the hydrotalcite precursor, different rehydration procedures (ex situ vs. in situ and liquid vs. gas phase) have been performed and their impact on the yield of the desired aldol condensation products has been determined. Moreover, the effect of the Mg/Al ratio has been studied as well.

2. Experimental and materials

2.1. Materials

Mg—Al layered double hydrotalcites (LDH) with Mg/Al molar ratio ranging from 2:1 to 4:1 were provided by Eurosupport Manufacturing Czechia (ESMC). One sample, denoted HTC-feed, was used as a reference material. Their properties and activation procedures are described below. Furfural (Acros Organics, 99%) and acetone (Lach:Ner, p.a.) were used in the experiments.

2.2. Catalysts activation

Three different activation procedures were applied to transform the as-supplied LDH materials into catalysts–calcination, ex situ rehydration of the calcined material and in situ rehydration of the calcined material. The calcination of LDH was performed at 450 °C in air and mixed Mg—Al oxide catalysts were obtained. The temperature during calcination was raised at the rate of 10 °C/min to reach 450 °C and maintained at the final temperature for 16 h. The calcined mixed oxides were used as catalysts in aldol condensation reaction directly or after rehydration.

The ex situ rehydration was carried out either in liquid or gas phase. The liquid phase ex situ rehydration was performed in a stirred flask using demineralized water at 20 °C for 2 h under inert atmosphere (N_2). After the activation, the catalyst was separated by filtration and dried under vacuum at 60 °C for 2 h. The gas phase ex situ rehydration was carried out in a glass tube at 50 °C under flow of nitrogen gas saturated with water vapor for 16 h. The flow of wet nitrogen of 6 L/h was maintained for the specified period (16 h for 5 g of catalyst). Both types of ex situ treatments lead to full rehydration of the calcined materials (mixed oxides). The amount of water needed for the full rehydration of the mixed oxides was approximately 1 g of water per 1 g of mixed oxides.

The in situ rehydration was carried out only in liquid phase. It was achieved by addition of a small amount of demineralized water (0.2 mL) into the reaction mixture before immersing the calcined catalyst into the reactor. In this case, approximately 10% wt. of the mixed oxides was rehydrated.

The list of all tested catalysts including their names and activation procedure is shown in Table 1.

Table 1
List of the catalysts used for catalytic tests.

Catalyst name	Activation procedure
Cal. HTC-feed	Calcination
Cal. HTC 2:1	Calcination
Cal. HTC 3:1	Calcination
Cal. HTC 4:1	Calcination
ExWR HTC-feed	Full ex situ rehydration in liquid water
ExWR HTC 2:1	Full ex situ rehydration in liquid water
ExWR HTC 3:1	Full ex situ rehydration in liquid water
ExWR HTC 4:1	Full ex situ rehydration in liquid water
ExVR HTC-feed	Full ex situ rehydration in water vapor
ExVR HTC 2:1	Full ex situ rehydration in water vapor
ExVR HTC 3:1	Full ex situ rehydration in water vapor
ExVR HTC 4:1	Full ex situ rehydration in water vapor
InWR HTC-feed	Partial in situ rehydration in liquid water
InWR HTC 2:1	Partial in situ rehydration in liquid water
InWR HTC 3:1	Partial in situ rehydration in liquid water
InWR HTC 4:1	Partial in situ rehydration in liquid water

2.3. Catalysts characterization

The catalysts were characterized by several techniques to assess their structure, composition, surface area and pore volume. The crystallographic structures of dried LDH catalysts were determined by X-ray powder diffraction using a Philips MPD 1880, working with the Cu—K_α line ($\lambda = 0.154$ nm) in the 2Θ range of 5°–70° at a scanning rate of 2Θ of 2.4°/min. The elemental composition was determined by X-ray fluorescence using Philips PW 1401 equipped with an Rh RTG lamp. The UniQuant program was used to evaluate the results. The textural properties of the catalysts (specific surface area and pore volume) were measured by nitrogen physisorption at −196 °C using a Micromeritics ASAP 2020 surface area and porosity analyzer. The plausible leaching of the main metals (Mg, Al) from the catalysts into the reaction mixture during the reaction was evaluated by ICP–OES equipment.

Thermogravimetric analysis of the dried LDH catalysts was performed using a TA Instruments TGA Discovery series equipment and operating at heating ramp of 10 °C/min from room temperature to 900 °C in flowing nitrogen (20 mL/min, Linde 3.0). Approximately 15 mg of sample was heated in an open alumina crucible.

2.4. Reaction studies

The experiments were carried out in a 100 mL stirred batch reactor (a glass flask reactor for experiments at up to 50 °C, an autoclave for experiments at temperatures above 50 °C) in liquid phase. Before the start of an experiment, 2 g of catalyst was mixed together with a stirred mixture of 39.5 g acetone and 6.5 g furfural (acetone/furfural molar ratio 10:1, pre-heated to the desired reaction temperature in range from 20 to 100 °C) and kept at this temperature for 2 or 24 h under intensive stirring.

The experiments were carried out at the strictly controlled conditions. Every time the same heating rate of 5 °C per minute was used. The experiments carried out at up to 50 °C were performed with the catalyst added into the reaction mixture after reaching of the reaction temperature. The experiments carried out at 100 °C were performed with the presence of catalyst in reaction mixture from the beginning of the heating. No overshooting of the target temperature was observed.

The used acetone/furfural molar ratio and the absolute amounts of the reactants could result, in the case of complete conversion of furfural, in the formation of approximately 0.8 g of water. This amount of water equals approximately to 40% of the amount needed for a full rehydration of the mixed oxides (calcined hydrotalcites).

The samples of reaction mixtures were withdrawn from the reactor during the experiment at certain reaction times, filtered, and analyzed by an Agilent 7890A gas chromatograph equipped with a flame ionization detector (FID), using a HP 5 capillary column (30 m/0.32 mm ID/0.25 μm).