



Short Communication

Unprecedented selectivities in aldol condensation over Mg–Al hydrotalcite in a fixed bed reactor setup



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ABSTRACT

Aldol condensation of furfural with acetone (molar ratio 1:10) was carried out in a flow fixed bed setup at 50 °C using calcined hydrotalcite with Mg/Al of 3 as a catalyst. Complete conversion of furfural and stable catalyst performance was obtained during the initial 50 h on stream. This period was followed by a rapid catalyst deactivation. In contrast to previous reports, higher molecular weight products that were identified as products of successive aldol condensation of acetone with furfural were observed. Their concentration was time-dependent with a maximum formation after 10 to 30 h on stream.

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1. Introduction

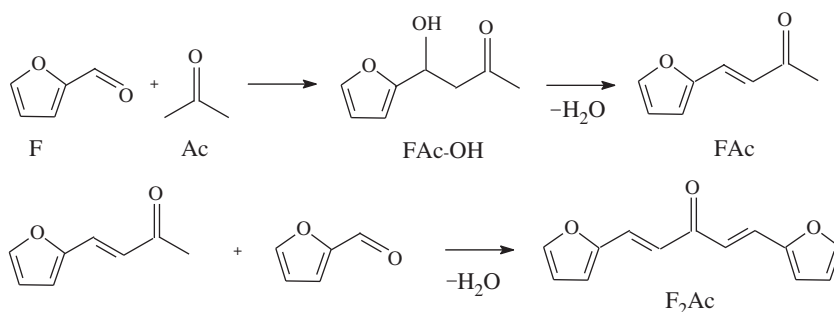
Biomass-derived short-chain aldehydes and ketones originating from pyrolysis of lignocellulosic biomass have rather limited direct applicability. Aldol condensation has been proposed to valorize these primary products by combining them into more complex reaction products with higher molecular weight. The reaction between furfural and acetone, which are suitable model compounds, results in the formation of ketones with 8 or 13 carbon atoms [1] (Scheme 1). Moreover, acetone molecule can interact not only with aldehydes (e.g. furfural) but also with ketones, hence also with another acetone molecule. This acetone self-condensation produces compounds with 6 or 9 carbon atoms [2]. Both acetone self-condensation and aldol condensation of furfural and acetone can be competitive reactions and proceed over the same catalyst at the same reaction conditions [1]. Industrially, homogenous base catalysts, such as sodium and calcium hydroxide, are used for aldol condensation. However, due to ecological and economic considerations the introduction of heterogeneous basic catalysts becomes very relevant [3]. Among these catalysts, layered double oxides, for example hydrotalcites (HTC), seem to be the most promising [4]. Calcined Mg–Al hydrotalcites possess high activity in the aldol condensation of furfural and acetone even at reaction temperatures below 100 °C [1]. Aldol condensation over heterogeneous basic catalysts, similar to a homogeneous process, is usually investigated in a batch reactor (a glass reactor or an autoclave) equipped with a stirring system. Nevertheless, to our best knowledge no information has been provided to date on the behavior of HTC as a catalyst for the aldol condensation between furfural and acetone in

flow reaction systems which are more favorable from a practical point of view. Moreover, only the application of a flow reactor system makes it possible to investigate the long-term stability (durability) of HTC materials in aldol condensation, which is essential for evaluating their prospects in industrial applications. In the present work we have studied aldol condensation of furfural and acetone using a flow reactor system with a fixed bed of a catalyst, a Mg–Al hydrotalcite with a molar ratio of Mg:Al = 3:1 calcined at 450 °C.

2. Experimental

Mg–Al layered double HTC with a Mg:Al molar ratio of 3:1 was prepared according to a procedure described in [1]. The crystallographic structure of the dried HTC catalyst was determined by X-ray powder diffraction using a Philips MPD 1880 instrument. Aldol condensation of furfural and acetone was carried out in a fixed-bed continuous-flow reactor with a catalyst loading of 10 g. The catalyst with a particle size of 0.125–0.150 mm was placed in the isothermal zone of the reactor, activated at 450 °C for 16 h under nitrogen flow, and then cooled down to 50 °C. The liquid feed, consisting of furfural (Acros Organics, 99%) and acetone (Lach:ner, p.a.) in the molar ratio of 1:10 was fed into the reactor by a micro-metering pump at weight hourly space velocity (WHSV) of the total reaction feed equal to 2 h⁻¹. The reaction conditions were $T = 50$ °C and $P = 0.5$ MPa. During the experiment, liquid reaction products were withdrawn from a cooler-condenser ($T = 0$ °C) every 2 h, weighed and analyzed by an Agilent 7890A GC equipped with a flame ionization detector and an HP-5 capillary column (30 m/0.32 mm ID/0.25 μm). The yield of liquid products during the experiment was 98% which can be explained by losses due to acetone evaporation. Finally, the carbon balance in GC analyses was calculated

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Scheme 1. Reaction pathways of aldol condensation of furfural and acetone showing only the main products.

as the number of carbon atoms analyzed in each GC sample (C3, C5, C8, C13, etc.) divided by the number of carbon atoms (C3 and C5) in the feedstock.

3. Results and discussion

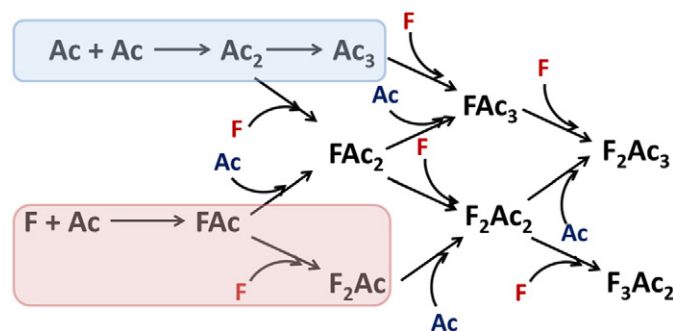
In accordance with the generally accepted reaction route, aldol condensation of furfural and acetone over basic catalysts results in the successive formation of the following reaction products: FAc-OH, FAc and F₂Ac (Scheme 1). GC analyses of mixtures obtained under flow reaction conditions revealed, however, the presence of additional reaction products. Their combined selectivity was as high as 35%. Using GC-MS analysis the following molecular weights (MWs) of the unknown products were established: 176, 218, 254, 272, 312 and 350. By combining the MWs of acetone and furfural while taking into account that furfural and acetone can interact not only with each other, but also with the products of acetone self-condensation and the main aldol condensation products, i.e. FAc-OH, FAc and F₂Ac, it was possible to identify plausible until now unknown reaction products. The classical products of the aldol condensation of furfural and acetone (FAc-OH, FAc and F₂Ac) can participate in the successive condensation reactions either with furfural or with acetone owing to the presence of α -H atoms in their structure. Based on the GC-MS results, the formation of the following products can be deduced: FAc₂ (MW 176), FAc₃ (MW 218), F₂Ac₂-OH (MW 272), F₂Ac₂ (MW 254), F₂Ac₃ (MW 312) and F₃Ac₂ (MW 350). Moreover, the involvement of acetone self-condensation products in aldol condensation with furfural is probable as well as these by-products were found in the reaction products too. The reaction between furfural and Ac₂ or Ac₃ would yield FAc₂ (MW 176) and FAc₃ (MW 218), respectively. The verification of both the exact molecular structure of these products and the proposed reaction pathways leading to their formation is an objective of our forthcoming study. There is no doubt, however, that aldol condensation of acetone and furfural is more complex than the reaction route presented in Scheme 1, resulting in a large number of products having high molecular weight that have not yet been reported and that could be attractive as automotive fuel components or their precursors. A tentative simplified reaction network leading to the formation of these products is depicted in Scheme 2. As it will be shown further, these products might affect the long-term stability of the catalytic activity of HTC catalysts.

Fig. 1 shows that complete furfural conversion was obtained during the initial 45 h of TOS (Fig. 1(A)). The observed high activity of the HTC sample during a long period proves that aldol condensation can be successfully carried out using a flow reactor with a fixed catalyst bed. Nevertheless, after TOS = 45 h furfural conversion has rapidly decreased and reached ca. 50% after 64 h. This indicates a rapid HTC catalyst deactivation. Fig. 1 also shows changes in selectivity to the reaction products with the increasing TOS. These changes reflect the alteration of the catalyst performance with TOS. At the very beginning, the composition of reaction products is limited to two compounds, FAc and F₂Ac (Fig. 1), which is in accordance with the commonly accepted reaction scheme. The primary reaction product, FAc-OH, is completely absent

during the initial 45 h of TOS indicating good dehydrating properties of fresh HTC catalyst. FAc is the main reaction product of aldol condensation of furfural and acetone, and selectivity to this compound exhibits an intricate dependence on TOS. At the beginning of the experiment the selectivity to FAc is 62–63%; it decreases to 54% at TOS = 20 h but reaches a maximum value of 73–74% at TOS = 42–44 h, i.e. at the very end of the range of total furfural conversion. Further, as the conversion of furfural rapidly drops, FAc selectivity tends to decrease to 66–67%. Fig. 1(A) shows that this decrease is accompanied by an increase in selectivity to primary reaction product, FAc-OH, proving a weakening of the dehydrating properties of the catalyst and, accordingly, a reduction of its total activity. A consecutive interaction of FAc with furfural results in F₂Ac formation. Fig. 1(A) shows that the selectivity to this product is equal to 33% at the start of experiment, but decreases to 5.6% after 20 h of TOS. As TOS further grows, the selectivity to F₂Ac also increases followed by a stabilization at 16–18%.

The peculiar selectivity dependence can be attributed to the formation of heavier condensation products. Fig. 1(B) shows that the group of heavier condensation products, i.e. F₂Ac₂-OH, F₂Ac₂, F₂Ac₃ and F₃Ac₂, is almost absent in the reaction mixture at low TOS. Their selectivity increases with the increasing TOS and reaches a maximum value at TOS = 10–30 h followed by a continuous decrease. Finally, these compounds totally disappear in reaction products at TOS > 60 h. Fig. 1 shows that the selectivities to FAc and F₂Ac, on the one hand, and to F₂Ac₂-OH, F₂Ac₂, F₂Ac₃ and F₃Ac₂, on the other hand, can be described as “inverse volcano” and “volcano” curves, respectively. Apparently, the increase in F₂Ac₂-OH, F₂Ac₂, F₂Ac₃ and F₃Ac₂ formation takes place at the expense of FAc and F₂Ac formation in the range of TOS = 10–30 h.

The observed variation in the composition of the reaction products during the experiment clearly has to reflect a change in the properties of the catalyst. At the initial phase (0–4 h), the pre-calcined HTC sample promotes the formation of FAc and F₂Ac in accordance with the commonly accepted reaction route of the aldol condensation of furfural



Scheme 2. Tentative reaction network leading to the formation of heavier condensation products of furfural (F) and acetone (Ac). The shaded areas correspond to acetone self-condensation (blue) and the main reactions of furfural and acetone condensation (pink). For the sake of clarity, only dehydrated products are shown.

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