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Catalysis Communications



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

with a maximum formation after 10 to 30 h on stream.

Short Communication

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



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A R T I C L E I N F O

ABSTRACT

Article history: Received 23 May 2014 Received in revised form 15 August 2014 Accepted 1 September 2014 Available online 16 September 2014

Keywords: Aldol condensation Hydrotalcites Furfural Acetone

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.

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 deacti-

vation. 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

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 (MW350). 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. F_2Ac_2 -OH, F_2Ac_2 , F_2Ac_3 and F_3Ac_2 , 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 F_2Ac_2 , on the one hand, and to F_2Ac_2 -OH, F_2Ac_2 , F_2Ac_3 and F_3Ac_2 , on the other hand, can be described as "inverse volcano" and "volcano" curves, respectively. Apparently, the increase in F_2Ac_2 -OH, F_2Ac_2 , F_2Ac_3 and F_3Ac_2 formation takes place at the expense of FAc and F_2Ac 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.



Fig. 1. A–Furfural conversion and selectivity to main reaction -FAc, FAc-OH and F_2Ac . B–Selectivity to heavier reaction products.

and acetone (Scheme 1). In the course of the reaction water is formed as one of the products of dehydration of a reaction intermediate, FAc-OH.

According to [5], calcined hydrotalcites can be reconstructed back to a layered structure if put in contact with water and appropriate anions. A comparison of the XRD patterns of as-synthesized HTC, the material calcined at 450 °C and the catalyst after long-term run (Fig. 2), proves that during the reaction the reconstruction of MgO phase which is characteristic of the calcined material to the layered HTC structure really takes place. Also, rehydration enhances the catalytic activity of reconstructed HTC materials in base-catalyzed reactions, including aldol condensation [1,6–8]. Thus, water formed due to FAc-OH dehydration could induce the reconstruction of HTC and cause a Lewis-to-Brønsted site transformation resulting from the reaction of O^{2-} basic sites with H₂O



Fig. 2. XRD patterns of the initial as-synthesized hydrotalcite (A), calcined material (B) and catalyst after long-run test (C). \star –HTC phase, \blacktriangle –MgO phase.

[9]. This process results in the enhancement of the catalytic activity of base-catalyzed reactions, for which OH⁻ sites act as active Brønsted base sites [4,6,8,10]. Our results show that these Brønsted basic sites in the reconstructed material have a pronounced ability to activate α -H atoms in ketones thus promoting an additional formation of bulky compounds and changing the product selectivity. However, these strong basic sites have been recently suggested to be responsible for catalyst deactivation in this kind of reactions [2]. The formation of bulkier compounds than F₃Ac₂ and F₂Ac₃ determined by GC may be also expected due to the further interaction of reaction products. These bulkier compounds would be less prone to desorption from the HTC surface resulting in the gradual deactivation of the catalyst as the one observed here, i.e. due to restricting/preventing the access of reactants to active sites. Nonetheless, further investigations of the formation of the heavier compounds and particularly of their interaction with the catalyst surface are needed.

Important supporting information for the conclusions presented above can be obtained from detailed analysis of acetone transformation. Acetone conversion and selectivity to the products of acetone selfcondensation observed during the long-term run are shown in Fig. 3. The initial conversion of acetone is \approx 15% with its slight increase to 17% after 12–14 h of the experiment. This increase in catalyst activity can be again explained by HTC reconstruction due to its re-hydration and the formation of Brønsted basic sites, which appear to have an increased ability to the abstract the α -proton in acetone molecule. Acetone conversion remains constant during the next ca. 30 h followed by its sharp decrease, which is in line with the trend observed for furfural conversion. Moreover, as the acetone conversion is stable for about 40-45 h at around 15-17% it can be unequivocally concluded that under the selected reaction conditions the HTC catalyst exhibits stable activity followed by a sharp deterioration of the catalyst performance. This conclusion is supported by the comparison of the reported thermodynamic equilibrium of acetone self-condensation to mesityl oxide, which is ca. 20% at 120 °C [11], and the conversion to mesityl oxide and diacetone alcohol reported here, which is about 5% (Fig. 3). As a result, it is concluded that the acetone conversion is not limited by the thermodynamical equilibrium.

Ac₂-OH is the main product of acetone self-condensation with a selectivity of 23–27%, and this compound gives Ac₂ upon dehydration (the remaining converted acetone yields condensation products with furfural described above). Fig. 3 depicts the complex behavior of Ac₂ selectivity during the experiment. At the beginning of the run Ac₂ selectivity exceeds 5%, followed by a sharp decrease to <1% at TOS = 8–10 h. This drop in selectivity may be explained by the increased affinity of the freshly calcined HTC catalyst to interaction with water resulting in the formation of the reconstructed HTC material as proved by XRD (Fig. 2). As a consequence, at the initial time the equilibrium



Fig. 3. Acetone conversion and selectivity to the reaction products of acetone selfcondensation (the rest of selectivity is due to the formation of compounds of F + Acinteraction).

 $Ac_2OH \leftrightarrow Ac_2 + H_2O$ is shifted to the right. As the process of HTC reconstruction is completed, the formed material does not react with water as easily thus resulting in the drop of Ac_2 selectivity.

However, with the further increase of TOS Ac_2 selectivity starts to increase and attains 2% at TOS = 20 h. The observed increase in the dehydration ability of the catalyst reflects the gradual changes in the properties of the active sites in reconstructed HTC, possibly, due to the increase of their strength. Obviously, a detailed investigation of the change of the properties of calcined hydrotalcite during the reaction under flow reaction conditions requires a separate study.

The results presented in Figs. 1 and 2 show that the behavior of Ac₂ selectivity and selectivities to bulky products of acetone/furfural aldol condensation observed at TOS = 10–50 h is very similar. It could be concluded that the formation of these compounds takes place on the strong sites which are responsible for both Ac₂-OH dehydration and α -proton activation in ketones. However, the same sites could be also responsible for the formation of non-desorbed reaction products which result in catalyst deactivation and the sharp decrease of its activity after 50 h of TOS.

4. Conclusions

It has been demonstrated for the first time that aldol condensation of furfural and acetone under flow conditions over calcined hydrotalcite catalyst results in the formation on a much wider variety of products than those typically reported for aldol condensation in a batch setup. While total furfural conversion could be obtained over the initial 40 h on stream, this period was followed by sharp decrease in activity due to rapid catalyst deactivation. The heavier products were identified as successive condensation products of acetone and furfural and they could be plausibly exploited as valuable diesel fuel components, particularly after deoxygenation.

Acknowledgments

This publication is a result of project no. P106/12/G015 supported by the Czech Science Foundation which is being carried out in the UniCRE center (CZ.1.05/2.1.00/03.0071) whose infrastructure was supported by the European Regional Development Fund and the state budget of the Czech Republic.

References

- L. Hora, V. Kelbichová, O. Kikhtyanin, O. Bortnovskiy, D. Kubička, Catal. Today 223 (2014) 138.
- [2] L. Faba, E. Díaz, S. Ordóñez, Appl. Catal. B Environ. 142–143 (2013) 387.
- [3] W. Shen, G.A. Tompsett, K.D. Hammond, R. Xing, F. Dogan, C.P. Grey, W.C. Conner Jr., S.M. Auerbacha, G.W. Huber, Appl. Catal. A Gen. 392 (2011) 57.
- [4] D.P. Debecker, E.M. Gaigneaux, G. Busca, Chem. Eur. J. 15 (2009) 3920.
- [5] D. Tichit, B. Coq, Cattech 7 (2003) 206.
- [6] S. Abello, F. Medina, D. Tichit, J. Perez-Ramirez, X. Rodriguez, J.E. Sueiras, P. Salagre, Y. Cesteros, Appl. Catal. A 281 (2005) 191.
- [7] S. Abello, F. Medina, D. Tichit, J. Perez-Ramirez, J.C. Groen, J.E. Sueiras, P. Salagre, Y. Cesteros, Chem. Eur. J. 11 (2005) 728.
- [8] Y. Xi, R.J. Davis, J. Catal. 254 (2008) 190.
- [9] Y. Liu, E. Lotero, J.G. Goodwin, X. Mo, Appl. Catal. A Gen. 331 (2007) 138.
- [10] R.J. Chimentao, S. Abello, F. Medina, J. Llorca, J.E. Sueiras, Y. Cesteros, P. Salagre, J. Catal. 252 (2007) 249.
- [11] A.A. Nikolopoulos, G.B. Howe, B.W.-L. Jang, R. Subremanian, J.J. Spivey, D.J. Olsen, T.J. Devon, R.D. Culp, Catalysis of organic reactions", in: M.E. Ford (Ed.), Marcel Dekker, Inc, NY, 2001, pp. 533–543.