ChemCatChem

The European Society Journal for Catalysis

Chemistry Europe

European Chemical Societies Publishing

Supported by GECATS GERMAN CATALYSIS SOCIETY

Accepted Article

Title: Polyurethane as Novel Catalyst for the Propoxylation of Fatty Amines

Authors: Pia Mueller, Maria Fernanda Neira d'Angelo, and John van der Schaaf

To be cited as: *ChemCatChem* 10.1002/cctc.202000337

Link to VoR: https://doi.org/10.1002/cctc.202000337

WILEY-VCH

10.1002/cctc.202000337

Polyurethane as Novel Catalyst for the Propoxylation of Fatty Amines

Pia Müller[a], Maria Fernanda Neira d'Angelo[a] and John van der Schaaf*[a]

Abstract: The propoxylation of fatty amines is a crucial reaction in the industrial production of surfactants. Catalyzing this reaction has so far proven unrewarding due to severe selectivity losses. In this study, rigid foam-structured polyurethane, i.e., an extremely inexpensive material which has not been used as a catalyst ever before, shows an unprecedented catalytic activity during the in-flow propoxylation of octylamine. The foam cells contain bound hydroxyl and amine groups that result in a bi-functional catalyst able to destabilize the ring structure of propylene oxide, and thus catalyze further propoxylation of fatty amines. An outstanding 10-fold reduction of the residence time without any loss of selectivity is achieved with respect to the un-catalyzed process. Furthermore, the polyurethane foam showed stable time-on-stream performance up to 10 bar and 110 °C.

Propoxylated fatty amines are widely used as non-ionic surfactants, with a steady increase in industrial demand over the past six decades. Since the 1950's, the propoxylation of fatty amines has been known to proceed auto-catalytically (i.e., in the absence of an additional catalysts[1]) and is therefore performed semi-batch wise. Concerns about safety and product quality due to formation of side products under intensified or catalytic conditions have justified a lack of innovation in this field in the last decades. While a number of new reactor systems have been proposed[2–4], research about catalytic enhancement has proven futile for this system. Catalysts used in the ethoxylation of phenols and acids, e.g., hydroxide salts[5–7], zeolites [8,9] or organometallic compound[10], are not active enough nor selective in the amine process.

In our previous work, the butoxylation of dodecylamine was found to be auto-catalytic, being both the amine and hydroxyl groups in the formed products the active species.[11] It is generally understood that the reaction mechanism proceeds via destabilization of the epoxide ring in the presence of proton donating groups[12].Our work concluded that the amine group adds to the destabilizing effect, and interacts with the resulting species to forming an even more reactive intermediate than the epoxide alone with hydroxyl groups. In this study, a preliminary screening of various catalyst materials was added to the previously performed screening of homogenous catalysts (Table S2 in SI and Figure S8). The screenings reveal that, for the propoxylation and butoxyilation of fatty amines, the co-addition of catalysts containing both amine and alcohol groups (e.g. ethanol-ethylamine) is essential to significantly increase the reaction rate. While the single functionality did show some catalytic enhancement (e.g. PVA showed 1.5 times the activity of the blank), the bi-functionality prompted a much stronger catalytic enhancement (i.e., 16 times the blank, Table S2 in SI). In this context, polyurethane foams containing the desired bi-functionality and showing an open cell structure that is ideal for heterogeneous catalysis became particularly attractive, and thus the focus of this study. While the effect of the hydroxyl groups (PU-OH) is clear, the role of the amine on the PU is yet uncertain. One possible explanations its involvement as a proton "shuttle" in the overall process, as the octylamine protons have to be transferred back to the newly deprotonated PU-OH groups (Figure 1).

As recently reviewed, polyurethane is a versatile material for manifold applications,[13] including catalytic support and as structural copolymer.[14–17] However, its use as catalytically active material has not been reported, to the best of our knowledge. Herein we report, for the first time, the use of rigid polyurethane foams (hereafter PU foam) as a bi-functional catalyst for the propoxylation of octylamine. The two catalytic active sites are as following:

1) hydroxyl groups, resulting from excess diols used in the formation of urethane groups.
2) amine groups, produced during foam blowing with water, which reduces isocyanates to amines and CO_2.

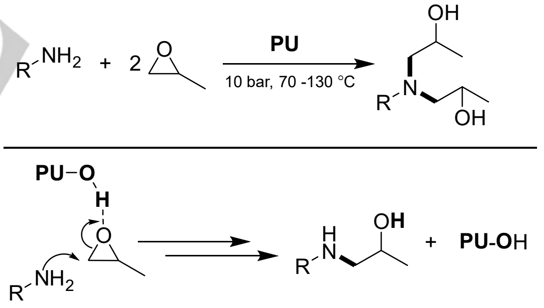


Figure 1. Propoxylation of fatty amines. Amine and alcohol groups destabilize the propylene oxide ring, thus increasing the effective collision. Epoxide ring opening catalysed by hydroxyl group of polyurethane.

The rigid PU foam with the tradename Tricast 5 was purchased from Goodfellow. According to mercury porosimetry measurements, the pore area is 1.87 m^2/g and the pore diameter is narrowly distributed around 2.5 µm. Initially, the foam contains over 95% closed cells, as reported by the purchaser. The supplied

---

[a] P. Müller Msc, Dr. M.F. Neira d'Angelo, Dr. J. van der Schaaf
Group of Sustainable Process Engineering ,
Department of Chemical Engineering and Chemistry
Eindhoven University of Technology
P.O. Box 513, 5600 MB Eindhoven (The Netherlands)
E-mail: j.vanderschaaf@tue.nl

Supporting information for this article is given via a link at the end of the document.

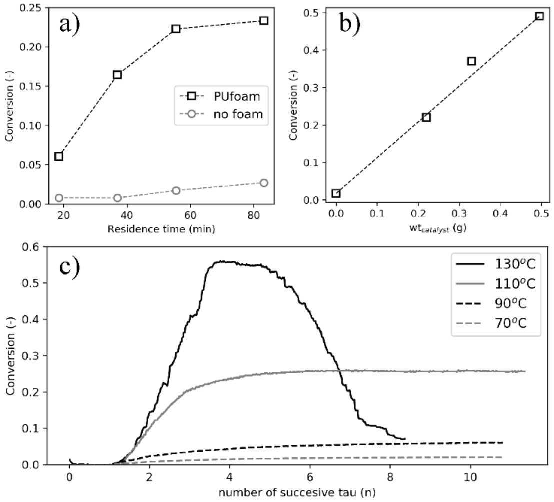


Figure 2. Conversion of propylene oxide in the reaction with octylamine versus (a) residence time at 90 °C and 0.22 g_{cat}; (b) weight of catalyst at τ= 55 min; (c) time-on-stream (expressed as number of successive cycles) and temperature at τ= 18 min and 0,22 g_{cat}.

foam is slightly basic (pH 9 in solution). For the catalytic tests, the as received PU foam is cut into cylinders with the dimensions of ø 7.5 x 10 mm (Figure 4a).
The catalytic activity of the PU foams during the propoxylation of octylamine is demonstrated by performing flow-through experiments in the ranges of 20 to 90 min residence time (Figure 2a), using a range of catalytic weight from 0 to 0.5 g of PU (Figure 2b), and temperatures from 70 to 130 °C (Figure 2c). The selectivity was in the pretest 0.95, in the flow experiments a selectivity of 0.99 was even observed. Figure 2a shows that, under same reaction conditions, the conversion increases by a factor 10 in the PU foam-catalyzed reaction with respect to the un-catalyzed benchmark at 90 °C. This could lead to a potential process intensification by reduction of reactor sizes or reaction temperature (e.g. from 180 °to 110 °C) to reach equal productivity.

Furthermore, the linear dependence of conversion on the catalyst weight (Figure 2b) clearly demonstrates that the PU foam acts as catalyst during this reaction. The strong dependence of conversion on temperature (Figure 2c) further suggests absence of (external) mass transport limitations. Although the maximum reaction rate is achieved at 130 °C (i.e., the highest temperature explored in this work), clear evidences of catalyst deactivation under these reaction conditions are observed. Below 130 °C, the PU shows stable catalytic performance during the total explored time-on-stream of 200 minutes.

The chemical stability of the PU foams is analyzed by FTIR (Figure 3). The spectrum of the as received PU foam corresponds to the spectra found in the polymers and plasticizers.[18] The main characteristic bands are marked in Figure 3.

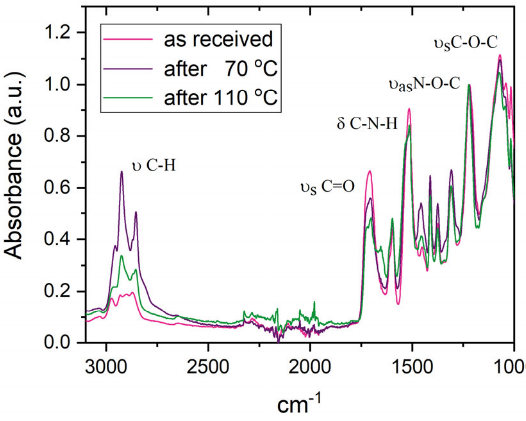


Figure 3. FTIR of PU foam normalized for as received foam and washed foam after reaction.

The used PU foams show similar FTIR spectrum, with additional peaks around 2800 cm^{-1} v(C-H), corresponding to the alkyl chain skeleton of residual octylamine and its products. A smaller peak around 1750 cm^{-1} v(C=O stretch) also appeared after the reaction at 110 °C, which Mishra et al. described, in regard to PU-urea-imide copolymers, as free and proton bond carbonyl groups.[15] In the reaction stream two additional absorption peaks were formed at 1030 and 1100 cm-1 after the conversion started dropping at 130 °C (> 90 min). These absorption overlap with the PU foams, amine and ether vibrations (Figure 3). Therefore showing only the decomposed PU particles flowing in the product stream. No other side or decomposition products were found (compare SI).These observations suggest that the PU foams are chemically stable until 70 °C and can be used as heterogeneous catalyst. During the reaction at 110 °C some degree of polymer chain cleavage occurs, breaking the urethane bond close to the carbonyl group.[19] At this point some contribution of homogeneous catalysts cannot be discarded entirely. Yet, the time-on-stream catalytic performance remains stable up to 110 °C (Figure 2c).
SEM images reveal that the initially closed foam cells (supplied with 95% closed cell, (Figure 4b), open upon exposure to flow conditions, even at room temperature, resulting in an open foam structure (<5% closed, Figure 4c). This mechanical opening of the foam structure at the start of the operation is believed to be beneficial for the catalytic activity since it improves the accessibility of the reactants to the active sites. The structural integrity of the open cell foams during operation was confirmed up to 110 °C by a stable time-on-stream catalytic performance (Figure 2c), and by visual inspection of the used foams after the reaction.

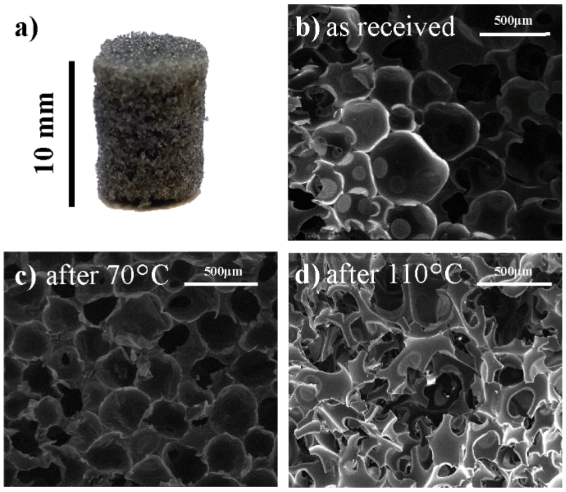


Figure 4. PU Foam. a) image of PU foam as used in reaction, b-d) SEM images of PU foam cells as received and used after reactions at two temperatures.

At even higher reaction temperatures, more severe structural changes take place (Figure 4d). While in tests at ambient conditions the PU foam proved catalytically stable over a period of more than a month, the loss of catalytic activity at 130 °C is attributed to: 1) thermal instability of the polyurethane foam,[20] which has an upper service temperature at around 90 °C; and/or 2) chemical instability caused by attack of propylene oxide and consequent decomposition of the polyurethane structure above 120 °C to polyols, ureas and amine species'.[19] Overall, the PU foam loses its structural integrity and reduces to particles smaller than 0.75 mm, thus passing through the filter at the reactor outlet, and impeding further characterization of the spent sample.

In conclusion, we have shown unprecedented catalytic activity of commercially available polyurethane foam on the propoxylation of octylamine; i.e., an industrially relevant reaction that could not be catalyzed selectively before. The catalytic activity of PU foam is attributed to the hydroxyl and amine groups present in the blown foam cells. The currently available polyurethane foams are not stable enough to operate at elevated temperatures (i.e., 130 °C and above) but show great potential to intensify the reaction without loss of selectivity up to 110 °C. While common methods to avoid or reduce catalyst degradation/deactivation involve modification of the process conditions,[21] in this case, further material development would likely be a more efficient solution. The design of a heterogeneous catalyst with the same hydroxyl and amino functionalities of the PU, but with increased thermo-chemical- stability at elevated temperatures, could potentially lead to a paradigm shift in the propoxylated amine production.

Experimental Section

The experiments were performed in a tubular reactor connected to a flow set-up. The foam was cut into cylinders and placed in the reactor separated by glass beads to avoid a large pressure drop. Both propylene oxide and octylamine were stoichiometrically mixed and pumped through the reactor, which was immersed in an oil bath. The backpressure of 10 bar guaranteed a one liquid phase mixture. The set-up was connected to an inline FTIR coupled with a sampling point for GC samples, leading to continuous process analysis. A more detailed description of the set-up, parts and chemicals can be found in the SI.

Acknowledgements

This research was carried out within the HighSinc program – a joint development between Nouryon Specialty Chemicals and the Department of Chemical Engineering and Chemistry from Eindhoven University of Technology. The authors thank T. di Martino for support in SEM data acquisition.

Conflict of interest

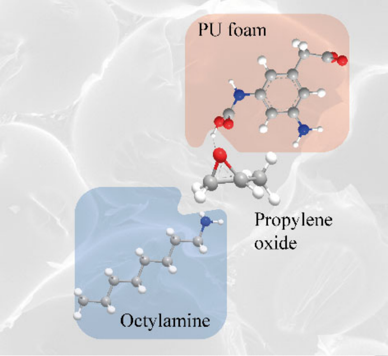
The authors declare no conflict of interest.

Keywords: amines • autocatalysis • epoxidation •heterogeneous catalysis • polyurethane foam

[1] S. Komori, T. Karaki, *Chem. Soc. Jpn.* **1959**, *62*, 538–542.
[2] L. L. van Dierendonck, J. Zahradnik, V. Linek, *Ind. Eng. Chem. Res.* **1998**, *37*, 734–738.
[3] M. Di Serio, R. Tesser, E. Santacesaria, *Ind. Eng. Chem. Res.* **2005**, *44*, 9482–9489.
[4] F. Sirovski, S. Mulyashov, V. Shvets, *Chem. Eng. J.* **2006**, *117*, 197–203.
[5] R. M. Laird, R. E. Parker, *J. Chem. Soc. B* **1969**, 1062–1068.
[6] M. Lukosek, K. Alejski, *Przem. Chem.* **2016**, *95*, 2352–2358.
[7] Y. N. Chiu, J. Naser, A. Easton, K. F. Ngian, K. C. Pratt, *Chem. Eng. Sci.* **2010**, *65*, 1167–1172.
[8] I. N. Senchenya, V. B. Kazansky, *Catal. Lett.* **1991**, *8*, 317–325.
[9] J. Trejbal, M. Petrisko, J. Pašek, *Pet. Coal* **2012**, *54*, 340–347.
[10] J. Herzberger, K. Niederer, H. Pohlit, J. Seiwert, M. Worm, F. R. Wurm, H. Frey, *Chem. Rev.* **2016**, *116*, 2170–2243.
[11] P. Müller, R. D. E. Krösschell, W. Winkenwerder, J. van der Schaaf, *Chem. Eng. J.* **2019**, 122939.
[12] J. W. Holubka, R. D. Bach, J. L. Andres, *Macromolecules* **1992**, *25*, 1189–1192.
[13] H.-W. Engels, H.-G. Pirkl, R. Albers, R. W. Albach, J. Krause, A. Hoffmann, H. Casselmann, J. Dormish, *Angew. Chem., Int. Ed.* **2013**, *52*, 9422–9441.
[14] L. Lefebvre, J. Kelber, L. Jierry, V. Ritleng, D. Edouard, *J. Environ. Chem. Eng.* **2017**, *5*, 79–85.
[15] A. K. Mishra, D. K. Chattopadhyay, B. Sreedhar, K. V. S. N. Raju, *Prog. Org. Coat.* **2006**, *55*, 231–243.
[16] P. A. Charpentier, K. Burgess, L. Wang, R. R. Chowdhury, A. F. Lotus, G. Moula, *Nanotechnology* **2012**, *23*, 425606.
[17] S. Gunashekar, N. Abu-Zahra, *Int. J. Polym. Sci.* **2014**, *2014*, DOI 10.1155/2014/570309.
[18] "Polymer Additives and Plasticizers Spectral Library," can be found under http://www.thermofisher.com/order/catalog/product/834-008300, **2018**.
[19] M. B. Sheratte, *Process for Converting the Decomposition Products of Polyurethane and Novel Compositions Thereby Obtained*, **1978**, US4110266A.
[20] D. K. Chattopadhyay, D. C. Webster, *Prog. Polym. Sci.* **2009**, *34*, 1068–1133.
[21] W. Wang, L. Cui, P. Sun, L. Shi, C. Yue, F. Li, *Chem. Rev.* **2018**, *118*, 9843–9929.

COMMUNICATION

Text for Table of Contents



*Pia Müller, Maria Fernanda Neira d'Angelo and John van der Schaaf**

Page No. – Page No.

Polyurethane as Novel Catalyst for the Propoxylation of Fatty Amines

Kitchen Sponge goes catalyst: Polyurethane foam was discovered as novel catalyst for production of nonionic surfactants by supporting the epoxide ring opening without side product formation. A conversion increase of a factor 10 was observed with a chemically stable foam till 110 °C.

Institute Twitter username: @TUe_ST