



Montmorillonite K10-induced decomposition of methyl *N*-phenylcarbamate to phenylisocyanate and its prospect for recovering isocyanates from polyurethanes[☆]

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Dedicated to Professor Manfred T. Reetz, on the occasion of his 80th birthday.

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ABSTRACT

The significant growth of the production and use of flexible polyurethane (PU) foam causes increased waste accumulation, thereby creating a demand for the recycling of PU. While upgrading PU materials to recycled polyols has been studied in detail, the recovery of diisocyanates is a longstanding challenge. Montmorillonite K10 (MK10) has been proposed as a catalyst to convert carbamates into isocyanates, but its prospects are unclear. Here, the MK10-catalyzed decomposition of methyl phenylcarbamate (MPC) into phenylisocyanate (PI) and the side product *N,N*-diphenylurea (DPU) has been studied as a model reaction for the decomposition of PU foam and the potential recovery of PI. The effects of the amount of catalyst, the temperature, and the solvent were investigated by HPLC analyses. Kinetic analysis revealed that the uncatalyzed rate of the MPC decomposition is much lower than the catalyzed rate, indicating that the thermally driven decomposition is negligible. Our results, involving both experimental kinetic studies and models of the kinetics, show that, while MK10 effectively catalyzes the decomposition of MPC, it also causes the formation of aniline, which reacts with PI to form DPU. As a result, large amounts of MK10 favor DPU and prevent the selective formation of PI, and yields of PI >30 % were never observed. Likely, the OH groups of MK10 form covalent bonds with PI, causing a deficiency in the mole balance. Overall, MK10 is unsuited to provide high yields of isocyanates.

Introduction

Polyurethane (PU) materials are an integral part of everyday life with a wide range of applications such as mattresses, insulation materials, and fibers for textiles [1–5]. The PU global market is expected to grow from 15 million tons in 2020 to 20 million tons by 2025 due to the expansion of the mattress, furniture, electronics, automotive, and construction industries [6]. In 1947, Otto Bayer first reported the polyaddition reaction of diols and diisocyanates to produce PUs [7,8]. Since then, PUs have been widely developed and diversified into a variety of applications [9]. However, with the significant growth of the PU industry, waste accumulation has risen, leading to a demand for the recycling of these materials. Recycling of PU by any selective

depolymerization is still economically challenging for the large-scale regeneration of the diisocyanates [10,11]. The most in-demand diisocyanates are methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI), followed by their aliphatic counterparts, such as hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) [12]. The alcoholysis of PUs delivers carbamates which can potentially be upgraded to diisocyanates for chemical recycling. Hence, reactions that could convert carbamates into isocyanates are of interest.

Most commonly, isocyanates are synthesized in the industry by phosgenation of an amine [13]. However, phosgene exhibits pronounced toxicity and generates hydrochloric acid as a byproduct, which is very corrosive. Several green alternative methods have been developed on a laboratory scale; however, few are economically competitive

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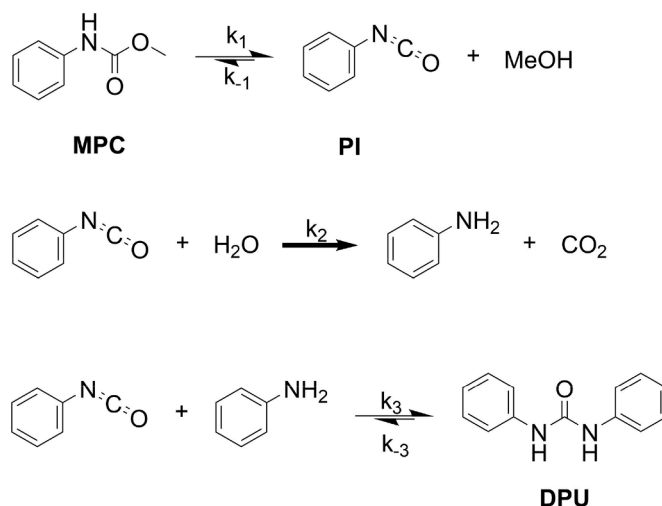
for the application. One such alternative method is the formation of carbamates by reaction with carbonate and its subsequent decomposition to isocyanates. The decomposition of methyl phenylcarbamate (MPC) to phenylisocyanate (PI) has been reported under several different catalytic conditions [14]. However, these studies are mostly focused on reagent conversion and did not provide mole balances, yields or side product analyses [15].

It was demonstrated by Zamani et al. that in closed systems, the thermal and catalytic elimination of MPC to PI is an equilibrium reaction favoring the carbamate at moderate temperatures, which provides a challenge to optimize the yield of the isocyanate [15]. In this study, it was reported that in a closed reactor, in which water cannot be removed, the catalyst hydrolyzed the PI, yielding aniline as the main product and forming *N,N'*-diphenylurea (DPU) as a side product, with no residual PI [15]. In contrast, catalytic elimination of MPC to PI in open systems holds the potential to remove water to suppress side product formation. Valli and Alper have reported a method of capturing the methanol with chlorocatecholborane and triethylamine as a simple and efficient way to drive the equilibrium to the isocyanate [16]. Although boron trichloride favors the isocyanate formation [17], sacrificial boron reagents are not affordable for industrial use. Alternatively, Dai et al. investigated the possibility of removing the alcohol by evaporation during the Bi_2O_3 -catalyzed decomposition of MPC in *o*-dichlorobenzene (ODCB), and produced PI in 78 % yield, with DPU [18]. Similarly, Uriz et al. reported an approach to the decomposition of MPC using the surface-active inorganic clay montmorillonite K10 (MK10) as an acidic catalyst with alcohol evaporation, in refluxing ODCB with a 96 % conversion of MPC [19]. However, neither the actual yields of PI and DPU nor the mole balance were given. This triggered us to study this reaction with a reflux system in more detail since MK10 is of potential interest for heterogeneous catalytic processes in industry [20].

The aim of this study is to investigate the decomposition of MPC to PI and side products, employing MK10 catalysis in ODCB under reflux conditions. We aim to answer the question whether or not MK10 has the potential to provide high enough yields of isocyanates to make it a suitable candidate for the conversion of carbamates into isocyanates in chemical industry. We target the integration of experimental work and kinetic modelling to provide detailed insight into the roles of MK10 in carbamate conversion and the promotion of side-reactions. To do so, the reaction was performed with varying amounts of MK10, and the conversion of MPC and its kinetics were monitored by HPLC. The temperature and solvent effects on the decomposition were also investigated. On the basis of the acquired information, a kinetic model was developed to provide further insight into the role of the MK10 catalyst in this reaction.

Results and discussion

The catalytic decomposition of MPC produces PI and methanol (Scheme 1). PI may react with traces of water to form aniline and CO_2 , and the aniline can then react with another equivalent of PI to form DPU. Under reflux conditions at the boiling point of ODCB (*i.e.*, at 180 °C), we expect that methanol and water are effectively removed from the reaction medium, at least to a large extent, allowing the build-up of PI. For the kinetic study of the decomposition of MPC to PI, aniline and DPU, a mixture of MPC and MK10 in ODCB was heated to 180 °C in a silicone oil bath for 3 to 9 h. Aliquots were taken at several designated times of 5, 30, 60, 120, 180, 300, 420, and 540 min. Basic product identification was performed by ^1H NMR comparing filtrate after reaction and the commercially available DPU (see Fig. S1). By varying the catalyst-reagent ratio, MK10:MPC (w/w) at 2, 1, 0.5, 0.3, and 0 (thermal) with exact masses of MK10 shown in Table S1, we studied its effect on the yields of both PI and DPU. To ensure maximum comparability, the same amount of solution (8 mL) and identical stirring conditions (800 rpm) were used in all experiments. All the aliquots for each MK10:MPC (w/w) experiment were taken at a comparable time series and analyzed by



Scheme 1. Decomposition of MPC to PI, aniline and DPU.

HPLC. Since isocyanates are highly reactive compounds, a derivatization reaction into 1,1-dibutyl-3-phenylurea (PI-DBA) was needed for reproducible HPLC analysis. The concentrations of PI, DPU, and unreacted MPC in the crude mixture were determined in order to assess the rates of decomposition of MPC and of formation of PI and DPU.

Fig. 1 shows the results of the MK10 catalyst dependence, by plotting the concentrations of MPC, PI, and DPU as a function of time. Although our HPLC setup was capable of detecting aniline, we did not observe any appreciable amounts of it. In the absence of MK10, the initial rates of change of all three species are significantly lower compared to those in the presence of MK10, confirming the catalytic effect of MK10. Fig. 1a shows that, for each catalyst-reagent ratio, the MPC concentration follows an exponential decay trend, with faster decay rates for higher amounts of catalyst. Thus, adding MK10 speeds up the decomposition of MPC proportionally. This catalytic effect of MK10 on the conversion of MPC has been observed before [19]. In contrast, as described above, it was reported by Zamani et al. [15] that water in MK10 hydrolyzed the PI in a closed reactor, yielding aniline as the main product at 200 °C. Overall, we conclude that our open system allows the formation of PI and largely prevents its hydrolysis to aniline, as was also observed by earlier studies.

Fig. 1b shows that, in the presence of MK10, the concentration of PI reaches a plateau after a certain period of time. The point at which the curves reach the plateau is affected by the ratio of MK10 to MPC. The more catalyst, the earlier the plateau is established. In particular at higher catalyst ratios (MK10:MPC (w/w) is 1 and 2), substantially less PI is produced. Fig. 1c shows that, in the presence of MK10, the concentration of DPU increases steadily following a linear trend, and the rate of change is increased proportionally with increasing ratio of MK10 present. Considering the fact that PI reaches a plateau while MPC decomposition and DPU production are ongoing, it can be concluded that PI is an intermediate to DPU. As a result, the formation of DPU from PI prevents the accumulation of PI over time. We note that the conversion into DPU is not sufficiently high to observe the expected decrease of PI after reaching the quasi-steady state. Additionally, as will be discussed below, the DPU may also equilibrate between aniline and PI [21], similar to the equilibrium between MPC, PI and methanol. The modest yields of PI are in contrast to what has been observed before [19].

Fig. 1d shows that the mole balance (based on aromatic moiety) for each MK10:MPC (w/w) ratio deviates from theoretical expectation. Loss of mole balance occurs even in the absence of catalyst, but is stronger at higher catalyst ratios. Assuming first-order kinetics for the MPC decomposition, the rate constant k_1 can be obtained from fitting the curves in Fig. 1a to an exponential decay function. The resulting rate constant k_1 is plotted as a function of the catalyst-reagent ratio (w/w) in

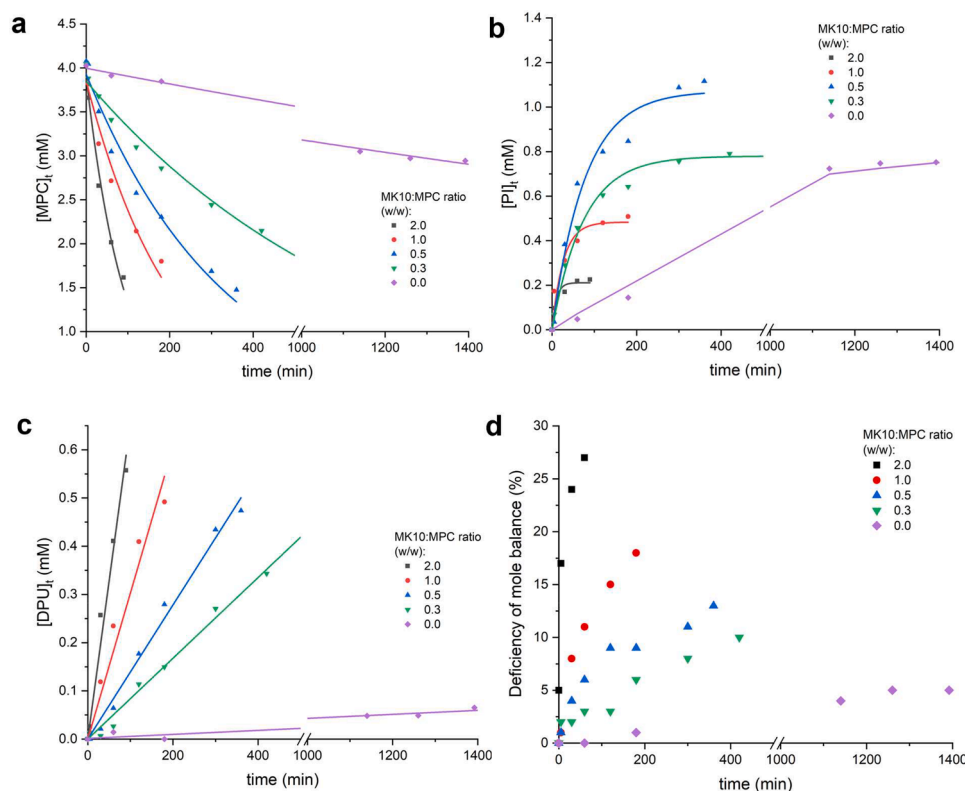


Fig. 1. Concentrations of MPC, PI, and DPU as a function of time, obtained from HPLC analyses of MPC decomposition experiments in ODCB, at 180 °C, in the presence of varying amounts of MK10. (a) Conversion of MPC, fits to 1st order kinetics. (b) PI formation fits to $[PI]_t = [PI]_S(1 - e^{-k_{PI}t})$, merely as a guide to the eye. (c) DPU formation, line fits of initial rates. (d) Deficiency of mole balance in time. The standard deviations for DPU yield, PI yield and mole balance were calculated as ± 0.07 , ± 0.06 , and ± 0.03 , respectively.

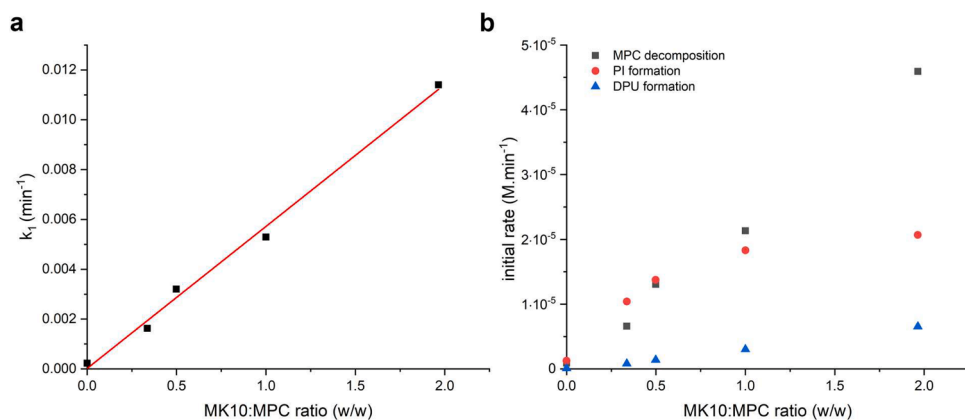


Fig. 2. (a) Initial rate constant k_1 of MPC decomposition as a function of MK10:MPC (w/w), fitted to: $k_1 = k_{1unc} + k_{1cat} \cdot x = 0.000018 + 0.0057x$, where x = the weight ratio w_{MK10}/w_{MPC} . (b) Initial rates of MPC decomposition, PI formation and DPU formation as a function of MK10:MPC (w/w) ratio.

Fig. 2a. The fitted line equation for k_1 gives the slope for the catalyzed contribution k_{1cat} equal to $0.0057 \pm 0.0002 \text{ min}^{-1} (w_{MK10}/w_{MPC})^{-1}$. The uncatalyzed rate constant k_{1unc} ($0.000018 \pm 0.000265 \text{ min}^{-1}$) was determined accordingly from the intercept of Fig. 2a. At all catalyst amounts used, k_{1unc} is much smaller than the catalyzed rate constant k_{1cat} of the MPC decomposition. Therefore, the contribution of the thermally driven decomposition is neglected.

Fig. 2b shows the initial rates of MPC decomposition, PI formation and DPU formation and exact initial rates of MPC, PI and DPU are shown in Table S2. The initial rate of MPC decomposition is linearly dependent on the MK10-MPC ratio, as already discussed. The initial rate of PI formation is equal to MPC decomposition at low catalyst amounts, but

levels off at high MK10:MPC. The initial rate of DPU instead is close to zero at low catalyst amounts but increases with MK10:MPC. The levelling off of the PI formation rate indicates that the formed PI is quickly removed by follow-up reactions, most likely to aniline and DPU. Since we do observe aniline neither in the reaction medium nor in Soxhlet extractions (see below), we conclude that any formed aniline may react away quickly to DPU. Alternatively, aniline may adsorb to the catalyst in ionic form, which could resist extraction. Based on these kinetic data, large amounts of MK10 prevent the selective formation of PI, as witnessed by the levelling off of its formation rate, and no large yields of PI can be obtained at any catalyst ratio. Worse, increasing amounts of catalyst have an increasingly detrimental effect on the production of PI,

as the catalyst apparently stimulates the follow-up reaction to DPU more strongly than it favors the conversion of MPC.

Fig. 3 shows the selectivity-conversion profiles of PI and DPU. From Fig. 3a, it is clear that modest amounts of catalyst do not affect the selectivity toward PI (although the rate goes up considerably with catalyst amount, for both PI and DPU formation, see Fig. 1). Only at the highest catalyst loadings, the formation of PI is negatively affected, in line with observations seen in Fig. 1b. From Fig. 3b, it appears that the induction time for forming DPU occurs at around 20–30 % conversion of MPC, regardless of catalyst amount. This indicates that aniline and PI are key contributors to the formation of DPU. The comparison between Fig. 3a and 3b indicates that, at MK10:MPC ratios of 1 and 2, the loss of PI selectivity does not lead to more pronounced formation of DPU, indicating that the loss of PI must lead to some other, undetected product.

Fig. 4 shows the deviation (deficiency) of the mole balance as a function of MPC conversion (a), PI yield (b) and DPU yield (c), as calculated by subtracting the experimental mole balance from the expected 100 %. It is evident that the mole balance deviates further from expectation with increasing amounts of MK10 present. In particular, as seen in Fig. 4a, when MK10:MPC (w/w) is 1 and 2, an increase in the deficiency of mole balance is observed compared to no or lower catalyst amounts. This may be rationalized by the adsorption (by physisorption or chemisorption) of PI or other products onto the surface of MK10 at the high catalyst ratios. To check for physisorption, Soxhlet extraction of the MK10 was performed after each experiment. In this way, only DPU could be recovered in mere trace amounts. So, physisorption of reagent or product does not appear to be a major issue, and hence does not explain the mole balance deficiency. Also washing of the condenser did not lead to significant amounts of trapped products.

Another possible reason for the deviation of the mole balance might be the presence of -OH groups on the MK10 surface that could covalently bind to PI (chemisorption). The possibility of a reaction between -NCO of PI and an -OH surface groups of MK10 has been reported by Xu et al. [22].

The possibility of carbamate formation by reaction of PI with the Si-OH groups of MK10 was investigated with FTIR (see Fig. S2). To test this, PI (0.6 mmol) was heated at 180 °C in ODCB in the presence of MK10 and the products were analyzed. After 2 h, 60 % PI and 26 % DPU were detected with an 86 % mole balance. As a control, PI was also heated in ODCB in the absence of MK10. After 2 h reflux, only PI was observed. In our experimental setup and analytical procedure, the formation of dimerization or trimerization species was not detected in the HPLC spectrum. It remains possible that trace amounts of these side products might have formed at 180 °C, but they were likely below the detection threshold of the HPLC system. This suggests that, within the parameters of our study, these side reactions were not a dominant feature of the

reaction process.

The FTIR spectrum of MK10 was acquired after the reaction, and a comparison was made with the initial MK10 spectrum. In Fig. S2, the emergence of a novel peak at 1705 cm^{-1} suggests the potential presence of a carbonyl group in a carbamate compound. A comparison with the FTIR spectra of aniline, DPU and MPC, with the reference carbonyl peak at 1755 cm^{-1} , typically associated with trimer isocyanate [23], strongly indicates the likelihood of carbamate formation. The observation supports the possibility of chemisorption, by reaction of PI to catalyst-OH groups, making this a plausible explanation for the observed mass balance loss at high catalyst amounts. Additionally, some peaks, notably those between 1300 and 1450 cm^{-1} (Fig. S2b), observed for the reaction of PI with MK10 overlap with those obtained by subjecting MK10 to aniline under reaction conditions. However, these signals do not seem to come from the ionic adsorption of protonated aniline (Fig. S2d). So, reaction of PI and of aniline with MK10 appears to lead to bound carbamate. Overall, we think the loss of mass balance has two components: The catalyst-independent mole balance loss is tentatively explained by the formation of a solid residue at the flask wall during each experiment (which was indeed observed occasionally but appeared very difficult to dissolve, thus escaping further analysis). In addition, the catalyst-dependent mole balance loss is attributed to chemisorption of PI (and aniline) to MK10.

To clarify the DPU formation pathway, the initial water content of MK10 was analyzed by TGA (Fig. S3). Despite all the efforts to dry the catalyst (at 300 °C for 12 h in a glass oven and keeping at 110 °C before use), TGA results of dried MK10 showed that some residual crystal water remains, possibly resulting from the transfer process of MK10 from the oven to the reaction vessel. This residual water may evaporate during ODCB reflux, and condense during the reaction at the glass surface of the reflux setup. However, aniline could not be detected in the reaction medium (detection limit < 3 %). This confirms that the water content present in MK10 and/or the setup at the reaction temperature is sufficiently high to react with PI to yield aniline, which then quickly reacts to DPU. Higher temperatures are essential to drive the MPC decomposition, since the reaction is endothermic and entropy-driven [15]. In order to determine the temperature effect on conversion and yields, three different reaction temperatures were investigated at MK10:MPC (w/w) = 1 for 9 h (Fig. S4). Only limited MPC conversion could be achieved in 9 h at 160 °C. Conversion increased significantly at 170 °C, while the highest conversion was achieved at 180 °C. In Fig. S4, also the yields of PI and DPU are given for the three different temperatures. At 160 °C, only trace amounts of PI and DPU were detected. At 170 °C, the same trend for the PI and DPU formation was observed. The best yield of PI was achieved at the boiling point of ODCB. The results from these three experiments support that the reaction temperature has a strong effect on the MPC decomposition and yield of PI. Nevertheless, as already

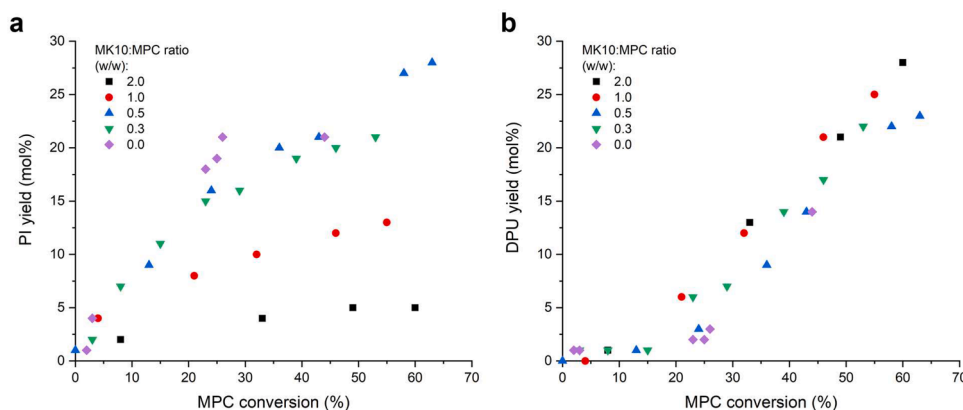


Fig. 3. (a) PI yield as a function of MPC conversion. Obtained from HPLC analyses of MPC decomposition experiments in ODCB, at 180 °C after 3 h, in the presence of varying amounts of MK10. (b) DPU yield as a function of MPC conversion.

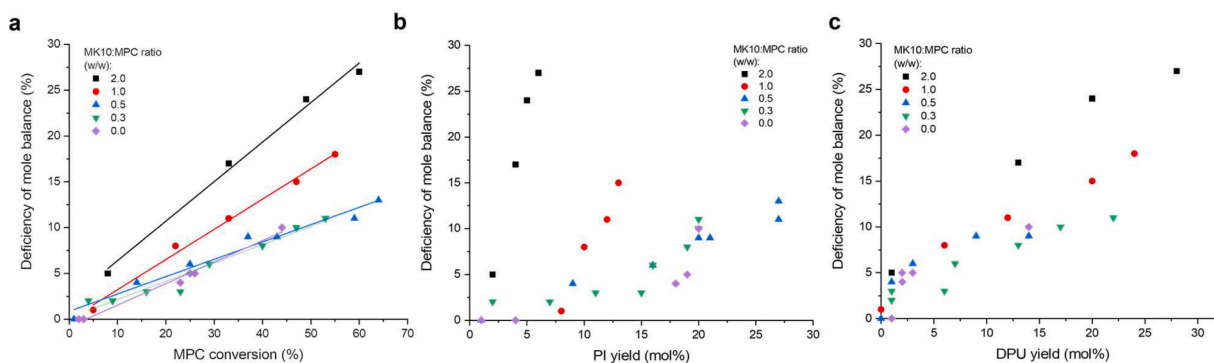


Fig. 4. Deficiency of mole balance as a function of (a) MPC conversion, (b) PI yield, and (c) DPU yield.

observed before, the yield of PI is never very high, which is attributed to the endothermic nature of the MPC decomposition.

We developed a kinetic model for the conversion of MPC to PI and DPU in ODCB, in order to fit the data presented in Fig. 1. The main considerations about which reaction steps to include and which rate equations to use, are provided in the Supplementary Information. All data sets at different catalyst amounts were fitted with a single set of parameters that were optimized in a least-squares minimization routine using the measured concentrations of MPC, PI, DPU and the mole balance. Moderate to excellent fits were obtained, see Figs S8 and S9 and Table S6. The conversion of MPC was fitted very well; the concentrations of PI and DPU somewhat less well. Yet, various trends were covered well, such as the lower plateau of PI at higher catalyst amounts, the slow ramp-up of the DPU concentration, and the lower mass balances at higher catalyst amounts. The fit was improved considerably when the back reaction from DPU to PI and aniline was introduced, hence we assume that also the formation of DPU is an equilibrium. We note that the model predicts the formation of small amounts of aniline; we assume that a fraction of it remains chemisorbed to the catalyst, as discussed above. Although Table S6 does provide the fitted model parameters with sensitivity intervals, we refrain from drawing further conclusions from these data, since no independent kinetic measurements were performed to target individual kinetic rate constants. Hence, the model should be seen only as a support for the observations and discussions provided above.

The model does not incorporate a concentration of free water explicitly. Attempts to do so failed, in large part because of the absence of real data on the water contents, and poorer fits were obtained. An alternative model to explain the formation of DPU by the disproportionation of two MPC molecules to DPU and dimethyl carbonate was ruled out. Although a decent overall fit of the data was obtained, the lag time of DPU formation was not reproduced. This is logical since the disproportionation is most favored at high MPC concentrations because of the second-order nature of the reaction, which should favor the fastest DPU formation at initial MPC conversion, which is evidently in contrast with observations.

The main difference between a closed and an open reaction vessel is the role of possible escape of volatile components, in particular water. As mentioned above, earlier work using a closed vessel has shown no PI but large amounts of aniline, in line with water remaining available for direct reaction with liberated PI. In contrast, the current and other studies have shown that open reactors with reflux conditions do show the formation of PI, and little to no aniline is observed. Yet, exactly how water is managed in such an open system remains unclear. Water adsorbed to the catalyst may evaporate during temperature increase before MPC conversion commences. Yet, water is necessary to explain the formation of DPU, which is attributed to hydrolysis of PI to aniline, followed by reaction with PI to DPU. It could be possible that some resides in the cooling section of the setup and flows back into the reaction vessel. However, implementing a molsieve section between the reaction

vessel and the condenser to bind gaseous water, did not show changes in the product mixture (data not shown). We therefore assume that some small amounts of water remain present inside the reaction mixture, possibly also chemisorbed to the catalyst, and potentially becoming available by reaction of PI to the catalyst's OH groups followed by dissociation of aniline from the chemisorbed catalyst-PI adduct. Further work will have to shed light on the presence and role of water in this reaction system.

Conclusions

Our general conclusion is that MK10 is unsuited as a catalyst for the recovery of isocyanates at larger scale. As explained above, PI was formed from the carbamate MPC, but its reaction yield never exceeded 30%. Conversely, high catalyst amounts favored the destruction of PI to DPU as well as chemisorption of PI to the catalyst. Obtaining closed mole balances appeared difficult; loss of mole balance appeared to have catalyst-independent and catalyst-dependent contributions, which are attributed to solid residue formation at the reaction flask and to chemisorption to the catalyst, respectively. The role of water in the process remains difficult to elucidate fully, as part of it may evaporate during reflux and part may remain available in the reaction mixture and/or chemisorbed to the catalyst. Overall, this work contributes to the understanding of isocyanate formation from carbamates, which is relevant for PU recycling. Different catalysts and more stringent water control will be necessary to achieve higher yields of isocyanates.

Experimental

Chemicals

Montmorillonite K10 (MK10, surface area 220–270 m²/g), *ortho*-dichlorobenzene (ODCB, 99%), acetonitrile (ACN; water < 30 ppm), dimethyl sulfoxide (DMSO, ≥ 99.9%), dibutylamine (DBA, ≥ 99.5%), trifluoroacetic acid (TFA), dimethyl sulfoxide-*d*₆ (DMSO-*d*₆, 99.9%), phenyl isocyanate (PI, ≥ 98%), 1,3-diphenylurea (DPU, 98%), poly(ethylene glycol) dimethyl ether (PEGDME, average Mn-250), dihydrolevoglucosenone (cyrene, ≥ 98.5%), 1-methylnaphthalene (1-MN, ≥ 95%), nitrobenzene (≥ 99%), and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU, ≥ 98%) were purchased from Sigma-Aldrich. Methyl *N*-phenyl carbamate (MPC) [24] and 1,1-dibutyl-3-phenylurea (PI-DBA, used for calibration of the HPLC) [20] were synthesized as described.

Methods and equipment

HPLC chromatography (Waters-2535) was performed with a column BridgeC18 5 μm (4.6 × 250 mm) with a UV-detector (2998 Photodiode Array Detector) at a wavelength of 240 nm.

The glassware was dried in an oven at 110 °C for 2 h. The catalyst

was dried at 300 °C for 12 h in a glass oven and kept at 110 °C in an oven before each experiment. All experiments were performed, under N₂ atmosphere, in a silicon oil bath and under ambient pressure. The MK10 sample was subjected to thermogravimetric analysis (TGA550, TA instruments). TGA was performed from 10 to 600 °C at a rate of 10 °C min⁻¹. FTIR spectra of MK10 before and after reactions were recorded in the range of 350–4000 cm⁻¹ on a Spectrum Two FTIR, PerkinElmer.

Experimental procedures

Catalyzed decomposition of MPC to PI and DPU

MK10 was dried at 300 °C for 12 h in a glass oven and kept at 110 °C in an oven before each experiment. Into a slurry of pretreated catalyst MK10 in ODCB (5 mL) in a 3-neck round bottom flask with an oil bath at 180 °C, a solution of MPC (100 mg) in ODCB (3 mL) was added. The final reaction volume in ODCB was 8 mL. Subsequently, the reaction mixture was heated while stirring at 800 rpm, and aliquots were taken at several designated times. Since isocyanates are highly reactive compounds, a derivatization reaction into a urea derivative was needed for stable analysis. For this purpose, PI was reacted with dibutylamine to give 1,1-dibutyl-3-phenylurea [25], which was added immediately after the sample collection. The aliquots were then analyzed using HPLC (30 min after sample collection) to determine the conversion of MPC, and the yields of PI and DPU. Prior to the HPLC injection, MK10 was separated from the sample mixture by PTFE syringe filters (HPLC-certified).

Analysis of HPLC calibration curves

The reaction progress was monitored with HPLC. In order to analyze the conversion and the yield of the compounds, calibration curves were made (Fig. S5) to pass through the origin of the coordinate. ODCB was selected as the internal standard in all the samples. The samples were formed mimicking the experimental samples with identical composition. A 10 mL stock solution was formed by mixing MPC, DPU, and PI-DBA into ACN with concentrations of 0.01 mmol/mL, 0.005 mmol/mL and 0.01 mmol/mL, respectively. The stock solution was mixed with ACN to 0.56 mL and then an extra 0.06 mL ODCB was added (Table S3). The resulting solution mixture was well mixed, whereupon 0.2 mL of it was extracted and diluted with 0.2 mL ACN. The sample preparation steps are shown in Fig. S6. In Fig. S7, the HPLC solvent system is shown. The ratios of MPC to ODCB, DPU to ODCB, and PI-DBA to ODCB were used as the y-axis of the calibration curves and the R² values of all the curves are presented in Table S4. The slopes of the curves are used to convert the HPLC signal of the designate compounds into their concentrations in every sample injection in Table S5. The reported carbamate conversion (X_{MPC}) in Eq. (1) is based on the content of MPC left in the HPLC injection given as I (in mmol), and the I_0 (in mmol) denoted as the starting amount of MPC quantified corresponding to the calibration curve.

$$X_{MPC} = (1 - I / I_0) * 100\% \quad (1)$$

The yield of PI, denoted as Y_{PI} , and that of DPU, given as Y_{DPU} , are shown in Eq. (2) and Eq. (3), respectively.

$$Y_{PI} = PI / I_0 * 100\% \quad (2)$$

$$Y_{DPU} = 2DPU / I_0 * 100\% \quad (3)$$

In Eq. (4), PI refers to the content of stabilized PI-DBA and DPU refers to the amount of DPU in the HPLC injection. The mole balance (M_b) consists of the quantity of MPC left in the injection, the amount of MPC converted into DPU and PI, which is shown in Eq. (4). Although the reaction between MPC to DPU can involve multiple reaction steps, the problem can be resolved by multiplying DPU by 2 to present a stoichiometric relationship between MPC and DPU.

$$M_b = (I + PI + 2DPU) / I_0 * 100\% \quad (4)$$

CRedit authorship contribution statement

Ege Hosgor: Data curation, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Chen-Kuan Lee:** Data curation, Writing – review & editing. **Nicola Capra:** Data curation, Methodology, Writing – review & editing. **Willem Verboom:** Supervision, Writing – review & editing. **Jean-Paul Lange:** Conceptualization, Funding acquisition, Methodology, Supervision, Writing – review & editing. **Jurriaan Huskens:** Conceptualization, Funding acquisition, Methodology, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare there is no conflict of interests.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mcat.2024.113930.

References

- [1] K. Błażek, J. Datta, Renewable natural resources as green alternative substrates to obtain bio-based non-isocyanate polyurethanes-review, Crit. Rev. Environ. Sci. Technol. 49 (2019) 173–211.
- [2] H. He, H. Su, H. Yu, K. Du, F. Yang, Y. Zhu, M. Ma, Y. Shi, X. Zhang, S. Chen, X. Wang, Chemical recycling of waste polyurethane foams: efficient acidolysis under the catalysis of zinc acetate, ACS Sustain. Chem. Eng. 11 (2023) 5515–5523.
- [3] P. He, H. Lu, H. Ruan, C. Wang, Q. Zhang, Z. Huang, J. Liu, Mechanochemistry: an efficient way to recycle thermoset polyurethanes, Polymers 14 (2022) 3277.
- [4] D.-S. Zhang, X.-H. Gu, S.-W. Liu, Y. Liu, O.-Y. Zhou, S.-W. Zhu, Y.-W. Zhu, Study on properties of regenerated fluorinated polyurethane rigid foam prepared by degrading waste polyurethane, Sustainability 14 (2022) 15685.
- [5] I. Amundarain, R. Miguel-Fernandez, A. Asueta, S. Garcia-Fernandez, S. Arnaiz, Synthesis of rigid polyurethane foams incorporating polyols from chemical recycling of post-industrial waste polyurethane foams, Polymers 14 (2022) 1157.
- [6] G. Kiss, G. Rusu, G. Bandur, I. Hulka, D. Romecki, F. Peter, Advances in low-density flexible polyurethane foams by optimized incorporation of high amount of recycled polyol, Polymers 13 (2021) 1736–1750.
- [7] O. Bayer, Das di-isocyanat-polyadditionsverfahren (polyurethane), Angew. Chem. 59 (1947) 257–272.
- [8] J. Banik, D. Chakraborty, M. Rizwan, A.H. Shaik, M.R. Chandan, Review on disposal, recycling and management of waste polyurethane foams: a way ahead, Waste Manag. Res. 41 (2023) 1063–1080.
- [9] E. Delebecq, J.-P. Pascault, B. Boutevin, F. Ganachaud, On the versatility of urethane/urea bonds: reversibility, Chem. Rev. 113 (2013) 80–118.
- [10] B. Liu, Z. Westman, K. Richardson, D. Lim, A.L. Stottlemeyer, T. Farmer, P. Gillis, V. Vlcek, P. Christopher, M.M. Abu-Omar, Opportunities in closed-loop molecular recycling of end-of-life polyurethane, ACS Sustain. Chem. Eng. 11 (2023) 6114–6128.
- [11] J.-P. Lange, Managing plastic waste-sorting, recycling, disposal, and product redesign, ACS Sustain. Chem. Eng. 9 (2021) 15722–15738.
- [12] D. Randall, The Polyurethanes Book, Wiley-VCH, Weinheim, 2002.
- [13] J. March, Advanced Organic Chemistry: Reactions, Mechanisms and Structures, Wiley-Interscience, New York, 1993.
- [14] G. Zhu, H. Li, Y. Cao, H. Liu, X. Li, J. Chen, Q. Tang, Kinetic study on the novel efficient clean decomposition of methyl N -phenyl carbamate to phenyl isocyanate, Ind. Eng. Chem. Res. 52 (2013) 4450–4454.
- [15] S. Zamani, J.-P. Lange, S.R.A. Kersten, M.P. Ruiz, Polyurethane recycling: conversion of carbamates-catalysis, side-reactions and mole balance, Polymers 14 (2022) 4869.
- [16] V.L.K. Valli, H. Alper, A. Simple, Convenient, and efficient method for the synthesis of isocyanates from urethanes, J. Org. Chem. 60 (1995) 257–258.
- [17] D.C.D. Butler, H. Alper, Synthesis of isocyanates from carbamate esters employing boron trichloride, Chem. Commun. (1998) 2575–2576.

- [18] Y. Dai, Y. Wang, J. Yao, Q. Wang, L. Liu, W. Chu, G. Wang, Phosgene-free synthesis of phenyl isocyanate by catalytic decomposition of methyl N-phenyl carbamate over Bi_2O_3 catalyst, *Catal. Lett.* 123 (2008) 307–316.
- [19] P. Uriz, M. Serra, P. Salagre, S. Castillon, E.A. Fernandez, A new and efficient catalytic method for synthesizing isocyanates from carbamates, *Tetrahedron Lett.* 43 (2002) 1673–1676.
- [20] L. Bieseki, F. Bertella, H. Treichel, F.G. Penha, S.B.C. Pergher, Acid treatments of montmorillonite-rich clay for Fe removal using a factorial design method, *Mater. Res.* 16 (2013) 1122–1127.
- [21] S. Zamani, S.H.E. van der Voort, J.-P. Lange, S.R.A. Kersten, M.P. Ruiz, Polyurethane recycling: thermal decomposition of 1,3-diphenyl urea to isocyanates, *Polymers* 15 (2023) 2522.
- [22] J. Xu, L. Cheng, Z. Zhang, L. Zhang, C. Xiong, W. Huang, Y. Xie, L. Yang, Highly exfoliated montmorillonite clay reinforced thermoplastic polyurethane elastomer: in situ preparation and efficient strengthening, *RSC Adv.* 9 (2019) 8184–8196.
- [23] J. Tang, T. Mohan, J.G. Verkade, Selective and efficient syntheses of perhydro-1,3,5-triazine-2,4,6-triones and carbodiimides from isocyanates using ZP ($\text{MeNCH}_2\text{CH}_2$)₃N catalysts, *J. Org. Chem.* 59 (1994) 4931–4938.
- [24] J.S. Martin, C.J. MacKenzie, D. Fletcher, I.H. Gilbert, Characterizing covalent warhead reactivity, *Bioorg. Med. Chem.* 27 (2019) 2066–2074.
- [25] E. Milchert, W. Paidzloch, Determination of ethyl N-phenyl carbamate, 4,4'-methylenebis(ethyl phenylcarbamate) and 4,4'-methylenebis(phenyl isocyanate) by high-performance liquid chromatography, *Analyst* 119 (1994) 1493–1495.