

Evaluation of Manganese Catalysts for the Hydrogenative Deconstruction of Commercial and End-of-Life Polyurethane Samples

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Polyurethane (PU) is a thermoset plastic that is found in everyday objects, such as mattresses and shoes, but also in more sophisticated materials, including windmills and airplanes, and as insulation materials in refrigerators and buildings. Because of extensive inter-cross linkages in PU, current recycling methods are somewhat lacking. In this work, the effective catalytic hydrogenation of PU materials is carried out by applying a catalyst based on the earth-abundant metal manganese, to give amine and polyol fractions, which represent

the original monomeric composition. In particular, Mn-^{Ph}MACHO is found to catalytically deconstruct flexible foam, molded foams, insulation, and end-of-life materials at 1 wt.% catalyst loading by applying a reaction temperature of 180 °C, 50 bar of H₂, and 0.9 wt.% of KOH in isopropyl alcohol. The protocol is showcased in the catalytic deconstruction of 2 g of mattress foam using only 0.13 wt.% catalyst, resulting in 90% weight recovery and a turnover number of 905.

Introduction

Polyurethane (PU) is a highly valued thermoset plastic formed by reacting an isocyanate with polyols.^[1] It represents one of the most widely applied thermoset plastics due to its myriad of different forms, which include rigid-, flexible-, and molded foams, elastomers, and adhesives.^[2] The characteristics of each PU material is a result of a careful choice of polyols, isocyanates, and additives. Owing to its easy manipulation and tailored design, PU is found in a plethora of different products ranging from refrigerators, mattresses, and shoes, to more sophisticated materials exploited in wind-blades and as components within the automotive and aviation industry.^[3] With a global PU production in 2020 estimated to 22 million tons, the lack of good recycling methods results in vast amounts of PU waste each year, of which most is sent for energy recovery through incineration.^[4,5] Although some energy is recovered, incineration of PU is troublesome due to formation of toxic gases and the presence of fire-retardants in many foams, besides the obvious loss of carbon-based material.^[5–8]

Current mechanical recycling methods for PU consists of grinding the plastic waste products into a powder or fabricating rebound materials from regluing flexible foams.^[9] While mechanical recycling offers the material a second life, such processes do not represent long-term viable solutions as the secondary material ultimately ends up in landfills or is incinerated. On the other hand, chemical (or tertiary) recycling in the form of either hydrolysis, aminolysis or glycolysis provides a means of reverting the polymerization to provide non-virgin monomers, which can be reused for new PU materials.^[5,10] To date, a few chemical recycling methods exist for PU deconstruction, however, only glycolysis is currently utilized on an industrial scale, albeit mainly contaminant-free PU waste is recycled just for the recovery of the polyol fraction.^[11–13]

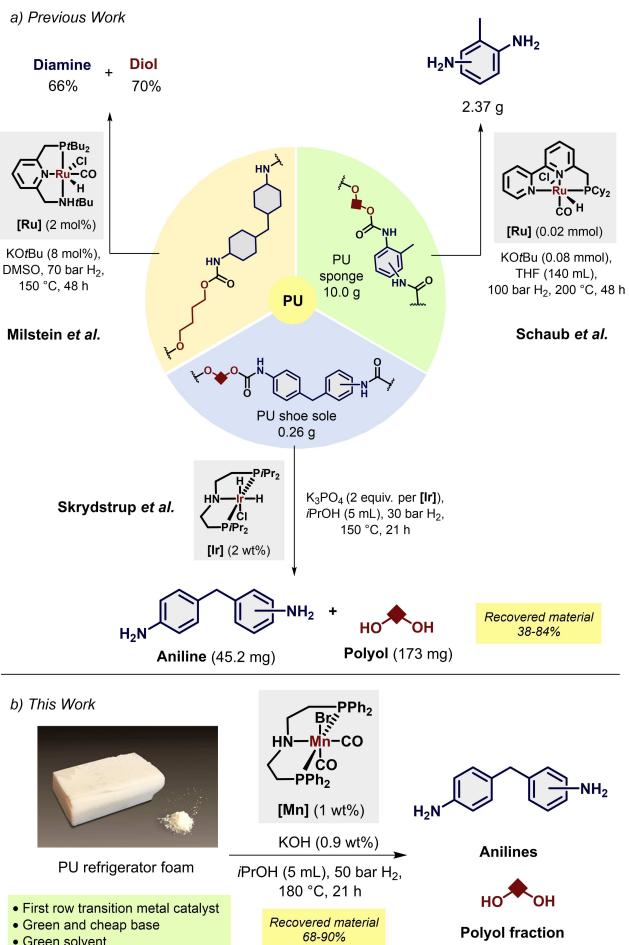
Recently, another chemical recycling strategy in the form of catalytic hydrogenation for the deconstruction of various polymers has gained more attention. Several homogenous transition metal catalysts have successfully been employed in lab-scale hydrogenation of carbonyl containing polymers, such as polyesters,^[14–18] polycarbonates,^[19–24] and polyamides.^[25] Methods for the catalytic hydrogenation of PU plastics to diamines and polyols have also started to emerge. Last year, Milstein and co-workers published a catalytic deconstruction of a PU resin, while the group of Schaub reported a method for the catalytic deconstruction of model and technical-grade PU materials. Both catalytic processes were based on the use of PNN ruthenium catalysts for the catalytic hydrogenation (Scheme 1a).^[25,26] Subsequently, we demonstrated the catalytic hydrogenation of a wide variety of PU materials covering all four PU cornerstones (rigid solid, rigid foamed, flexible solid and flexible foamed), employing the commercially available Ir-^{Pr}MACHO catalyst (Scheme 1a).^[27]

In our efforts to identify more sustainable catalysts based on earth abundant metals, which demonstrate high activity for

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Scheme 1. Catalytic hydrogenation of PU samples using ruthenium (Milstein and Schaub),^[25,26] iridium (Skrydstrup),^[27] and manganese (this work).

the hydrogenative deconstruction of end-of-life PU commercial products, we turned our attention towards manganese.^[28] Representing the third most abundant transition metal in the earth's crust (after iron and titanium), the biocompatibility of manganese with low toxicity and as part of metabolic processes has made this particular metal an interesting substitute for noble metals.^[29] Since the seminal reports by the groups of Beller and Milstein in 2016, the use of Mn-based pincer complexes for catalytic (de)hydrogenation has increased tremendously.^[30,31] Numerous methodologies for the hydrogenative cleavage of C–O, C–N and C–C bonds have been reported as summarized in a recent review.^[32]

Herein, we report on the identification and application of an efficient manganese-based catalyst, Mn-^{iPr}MACHO, for the catalytic deconstruction of polyurethanes to diamines and polyols using an inexpensive base (KOH), a green solvent (*i*PrOH) and dihydrogen (Scheme 1b). These results build on initial tests with Mn-^{iPr}MACHO for deconstruction of flexible foam reported by our group.^[27] This procedure offers a base metal alternative to ruthenium or iridium for catalytic hydrogenative depolymerization of PU, while a high efficiency and turnover is maintained. Most importantly, the catalyst was

demonstrated to effectively deconstruct four commercial PU products, representing different subclasses of this polymer.

Results and Discussion

Initial efforts were focused on studying the activity of various manganese catalysts for the catalytic hydrogenation of a linear PU model (**PU-1**), prepared from an isomeric mixture of both MDI (4,4'- and 2,4'-methylenedianiline) and dipropylene glycol. To this end, PPP-, PNP-, PNN-, NNN-based pincer catalysts and PP- and NN-based catalysts carrying bidentate ligands were synthesized and tested for catalytic activity in the hydrogenative deconstruction of **PU-1** using 2 wt.% catalyst, 2 equiv. of K₃PO₄ per [M], *i*PrOH (5 mL) as the solvent at 150 °C and 30 bar H₂ for 21 h (see Figure 1 and the Supporting Information, Section 6a for full details). Most of the catalysts tested gave low yields of the desired MDA (4,4'- and 2,4'-methylene diphenyl diamine). Whereas [Ru(triphos)tmm]NTf₂, was highly active for the hydrogenation of polyesters and polycarbonates, the corresponding Mn-TriPhos complex (**Mn-1**) displayed almost no activity for the catalytic deconstruction of **PU-1**.^[16] The Mn-PNP complexes **Mn-2-R** (R = *i*Pr, *t*Bu, Ph), previously reported as efficient catalysts for the α -alkylations of ketones, nitriles, esters and amides, and also for the preparation of pyrroles and aldimines, provided a low yield of only 3–4% of the amines for the *i*Pr- and Ph-substituted PNP, while the *t*Bu-substituted PNP catalyst exhibited no reactivity.^[30,33–37] Similar non-productive yields were obtained applying Mn-PN^{3P} (**Mn-3**), a catalyst exploited by Kempe and co-workers to afford pyrimidines in multicomponent synthesis.^[38]

Next, Mn-^{iPr}MACHO (**Mn-4**), a manganese complex reported to be efficient for upgrading EtOH to higher alcohols,^[39,40] was evaluated. This complex proved to be active for hydrogenating **PU-1** into its monomeric components, as a 67% yield of the desired MDA could be achieved. Interestingly, the similar iron-based catalyst, Fe-^{iPr}MACHO (**Fe-1**), previously employed in the hydrogenation of CO₂, esters, amides and nitriles, as well as in dehydrogenation reactions for the preparation of ketones, carboxylic acids, lactones and lactams,^[41,42] proved to be catalytically viable, although providing a lower yield (50% yield). As the ^{iPr}MACHO-based catalyst showed worthy activity for the hydrogenative cleavage of **PU-1**, it was intriguing to determine the effect of changing the oxidation state of Mn. For this reason, the pincer complex Mn^{II}-^{iPr}MACHO (**Mn-5**) was readily prepared from MnCl₂ (see the Supporting Information Section 3) and tested for the catalytic activity in the deconstruction of **PU-1**. Unfortunately, **Mn-5** displayed no significant activity, suggesting the importance of the stable low-spin Mn^I oxidation state with strong field CO ligands for catalytic efficiency.^[43]

Subsequently, a range of PNN-based Mn-pincer complexes (**Mn-6**,^[44–46] **Mn-7**^[47–49] and **Mn-8**,^[24,50–53]), known to perform well in challenging hydrogenations of amides and ureas amongst others, were evaluated for the catalytic hydrogenation of **PU-1**. Although, a recent study by Liu and co-workers would suggest PNN-based **Mn-6** and **Mn-7** to outperform PNP-based

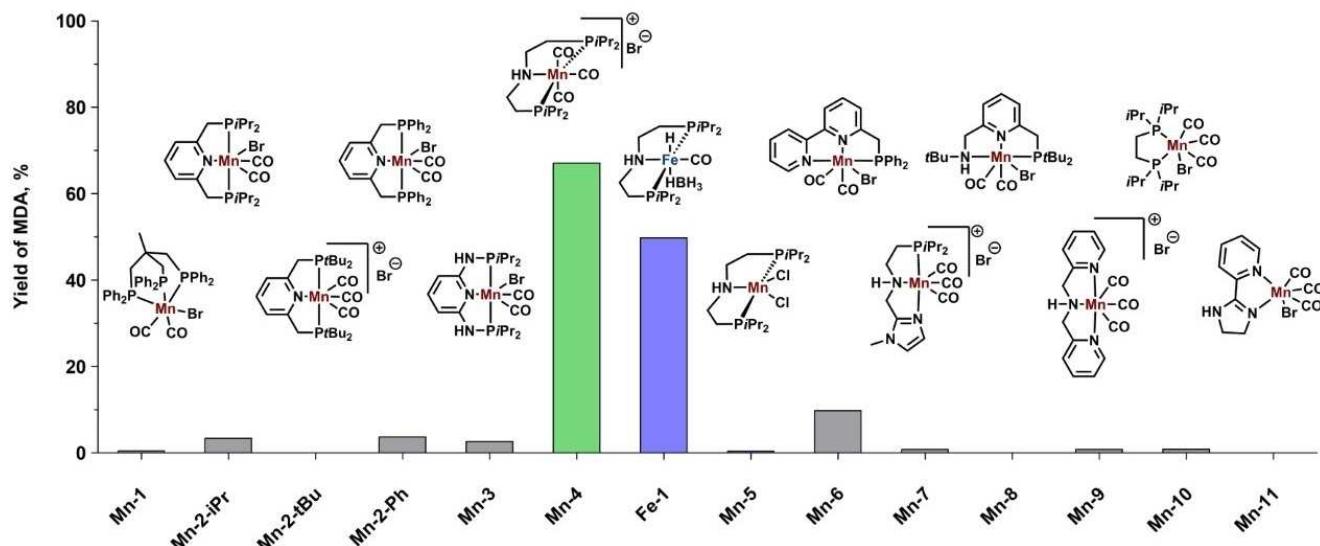


Figure 1. Assessment of Mn complexes for PU model reductions. All reactions were performed in a 45 mL autoclave fitted with a 30 mL poly(tetrafluoroethylene) inlay using 260 mg of ground PU-1, 2 wt.% of [M], 2 equiv. of K_3PO_4 per [M] in $iPrOH$ (5 mL) with 30 bar H_2 at 150 °C for 21 h. For **Mn-2-R**, 5 equiv. of $KOtBu$ per **Mn-2-R** was used instead. Yields of 4,4'-diamine and 2,4'-diamine were determined by GC-MS analysis. See the Supporting Information, Section 6a for full details.

Mn-^{iPr}MACHO (Mn-4), both **Mn-7** and **Mn-8** proved to be catalytically inactive under the tested conditions, while **Mn-6** provided only a low yield of the product (10%).^[54] Similarly, the NNN-type pincer complex, **Mn-9**, an efficient catalyst towards the hydrogenation of ketones,^[55] was not effective for cleaving carbamate bonds to an appreciable extent under these conditions. From here, the activity of a couple of bidentate PP- and NN-type Mn complexes (**Mn-10** and **Mn-11**), earlier reported for the hydrogenation of nitriles and the dehydrogenation of formic acid, were evaluated.^[56,57] However, both of these catalysts failed at deconstructing PU-1. Finally, the manganese complex precursor [$Mn(CO)_5Br$] and the free ligand (^{iPr}MACHO) were tested, resulting in no MDA formation (see the Supporting Information, Section 6a for full details).

As ^{iPr}MACHO-ligated **Mn-4** proved effective for the hydrogenation of PU-1, various alkyl substituted phosphorous-based MACHO ligands were assessed to probe their effect on the hydrogenation efficiency by changing the level of steric congestion around the metal center. Substituting the isopropyl groups (**Mn-4**) for cyclohexyl (**Mn-4b**) caused a significant decrease in activity as the yield of MDA was reduced from 67% to 35% (Figure 2). Since **Mn-4** and **Mn-4b** differ by the number of ligated carbon monoxides on the metal center, a comparison of **Mn-4** and **Mn-4a** was necessary. Interestingly, these catalysts performed equally well indicating that under the reaction conditions **Mn-4** is most likely to be transformed into **Mn-4a**. The complex **Mn-4c**, displaying ethyl groups, provided slightly better yields (76%). Delightfully, the diphenyl substituted derivative **Mn-4d**, provided an 84% yield of the MDA product. In contrast, the cationic complex **Mn-4e**, displaying bulkier *tert*-butyl groups, was completely inactive for the hydrogenation of

PU-1, which might suggest the inability of the substrate to reach the active metal center.

Methylation of the central amine functionality of the ligand backbone was also attempted, resulting in a complete loss of catalytic activity for the corresponding complex (Figure 2, **Mn-4f**). This outcome is consistent with a metal-ligand cooperation mechanism and in accordance with previously reported results using similar methylated Mn-MACHO pincer complexes.^[39,41,42,47,58–60] Another explanation for such inactivity was given by Gordon and co-workers who proposed that *N*-alkylation actually eliminates the possibility for hydrogen-bonding interaction between the substrate and the catalyst and increases steric hindrance around the active metal site, which in turn encumber hydride transfer to a carbonyl moiety.^[61]

Thereafter, the activity of **Mn-4d** was assessed under different conditions regarding base, solvent, dihydrogen pressure and catalyst loading. By utilizing stronger bases like $KOtBu$ or KOH 90- and 85% of MDA were observed, respectively (Table 1, entry 2 and 3). Subsequently, a less bulky alcohol in the form of EtOH was tested as solvent. Here, it was speculated that a base-catalyzed transcarbamoylation of PU-1 (or alcoholysis) might be faster with a primary alcohol, and hydrogenative cleavage of the resulting carbamate group might be more facile due to greater accessibility to the carbonyl functionality. Unfortunately, performing the reaction in EtOH using either K_3PO_4 , $KOtBu$ or KOH did not improve the yields of MDA (entries 4–6). As both KOH and $KOtBu$ provided similar or higher yields than K_3PO_4 , we eventually continued with KOH due to its significantly lower price. Here, it was observed that increasing the KOH loading to 5 equiv. per [Mn] resulted in a similar yield of 86% (entry 7).

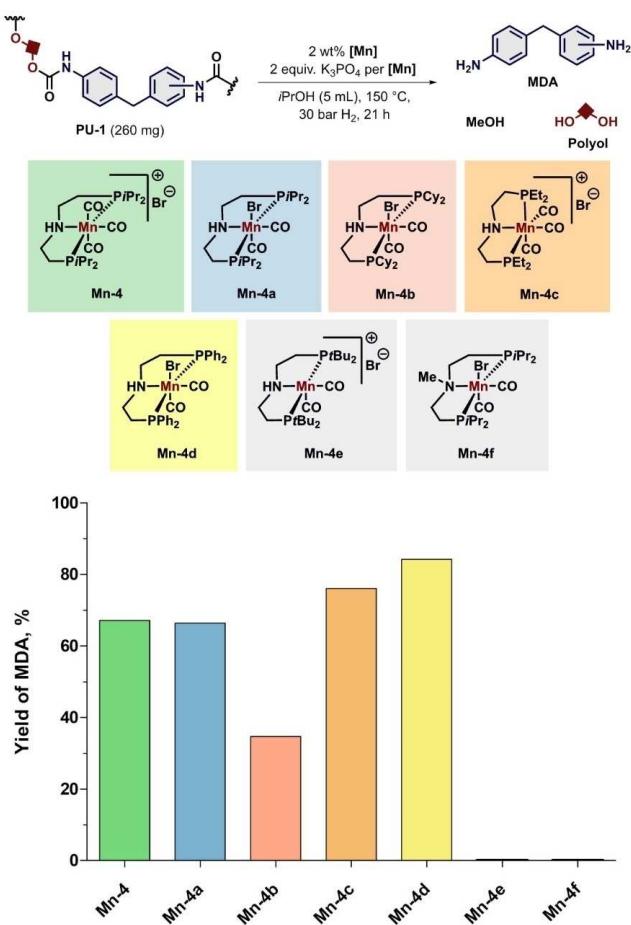


Figure 2. Catalytic hydrogenation of PU-1 using Mn-MACHO catalysts. All reactions were performed in a 45 mL autoclave fitted with a 30 mL poly(tetrafluoroethylene) inlay. GC-MS was used to determine the amount of 4,4'-MDA and 2,4'-MDA. Results are based on the average of two experiments.

Attempting to increase the turnover number of **Mn-4d**, the catalyst loading was reduced to 1 wt.% resulting in a 22% yield of the aniline (Table 1, entry 8). However, raising the temperature to 180 °C, while maintaining 1 wt.% catalyst loading, provided an appreciable yield of 69% (entry 9). This could be improved to a 76% yield when the KOH loading per [Mn] was increased to 10 equiv. (entry 10). By augmenting the pressure of dihydrogen to 50 bar, an 86% conversion to MDA was observed with 5 equiv. of KOH per [Mn], but an outstanding 92% yield was obtained with 10 equiv. of base per [Mn] (entries 11 and 12). From this latter result, a 92% yield of MDA could be isolated along with 92 wt.% of the original polyol. From the GC-MS analysis of the crude reaction mixtures (entries 1–13) methanol was observed, suggesting a reduction sequence potentially involving formamides and formaldehyde as intermediates (see the Supporting Information, Section 6c for full data). Lastly, to explore if any secondary effect was operating during the hydrogenation of PU-1, a few control experiments were carried out. As expected, without either the catalyst or

Table 1. Optimization of the catalytic hydrogenation of PU-1 using Mn-^{Ph}MACHO.^[a]

Entry	Deviations from standard conditions	Aniline ^[b] [%]
1	none	84
2	KO <i>i</i> Bu	90
3	KOH	85
4	EtOH	72
5	KO <i>i</i> Bu, EtOH	69
6	KOH, EtOH	63
7	5 equiv. KOH per [Mn]	86
8	1 wt.% [Mn], 5 equiv. KOH per [Mn]	22
9	1 wt.% [Mn], 5 equiv. KOH per [Mn], 180 °C	69
10	1 wt.% [Mn], 10 equiv. KOH per [Mn], 180 °C	76
11	1 wt.% [Mn], 5 equiv. KOH per [Mn], 180 °C, 50 bar	86
12	1 wt.% [Mn], 10 equiv. KOH per [Mn], 180 °C, 50 bar	92 (92) ^[c]
13	KOH, no H ₂	12
14	No catalyst, 0.9 wt.% KOH, 180 °C, 50 bar	2
15	No base, 180 °C, 50 bar	3
16	No catalyst, no base, 180 °C, 50 bar	0

[a] All reactions were performed in a 45 mL autoclave fitted with a 30 mL poly(tetrafluoroethylene) inlay using 260 mg of ground PU-1. Results are based on the average of two experiments. [b] GC-MS was used to determine the amount of 4,4'-MDA and 2,4'-MDA. [c] Isolated products.

base, the aniline yield was negligible. In the absence of dihydrogen, but with 2 wt.% [Mn], 12% of MDA could be observed indicating that a transfer hydrogenation mechanism from isopropyl alcohol was operating, albeit it proved to give variable yields. Omission of both catalyst and base resulted in no conversion (entries 13–16). While no alkylation of the amine product was observed, subjecting MDA to the optimized reaction condition did result in some degree of mono- and dialkylation of the aniline nitrogen (see the Supporting Information, Section 6f).

Based on the optimized reaction conditions for the catalytic hydrogenation of thermoplastic PU-1 employing 1 wt.% **Mn-4d**, 10 equiv. of KOH per [Mn] (or 0.9 wt.% KOH), 50 bar H₂ and 180 °C in *i*PrOH, a representative selection of commercial and end-of-life PU samples were tested (Figure 3). A flexible foam mattress (**PU-2**) was subjected to the optimized reaction conditions. To our delight, 99% of the original isocyanate in the form of the corresponding amine could be isolated along with 97 wt.% of the original 3000 MW polyol (see the Supporting Information, Section 4 for the recipe). Overall, this provided a satisfying 86% mass recovery, where the remaining 14% could mainly be attributed to the different additives from the polymerization process, and mass loss in the form of MeOH from hydrogenated carbamate functionalities. For **PU-2** with full conversion to anilines and polyol, the purification of the different fractions could also be obtained from a simple acid/base extraction procedure (see the Supporting Information, Section 5). A final experiment was made, where a 1:1 mixture **PU-1** and **PU-2** (260 mg) was subjected to the catalytic hydrogenation conditions. Here too, both polymers could be

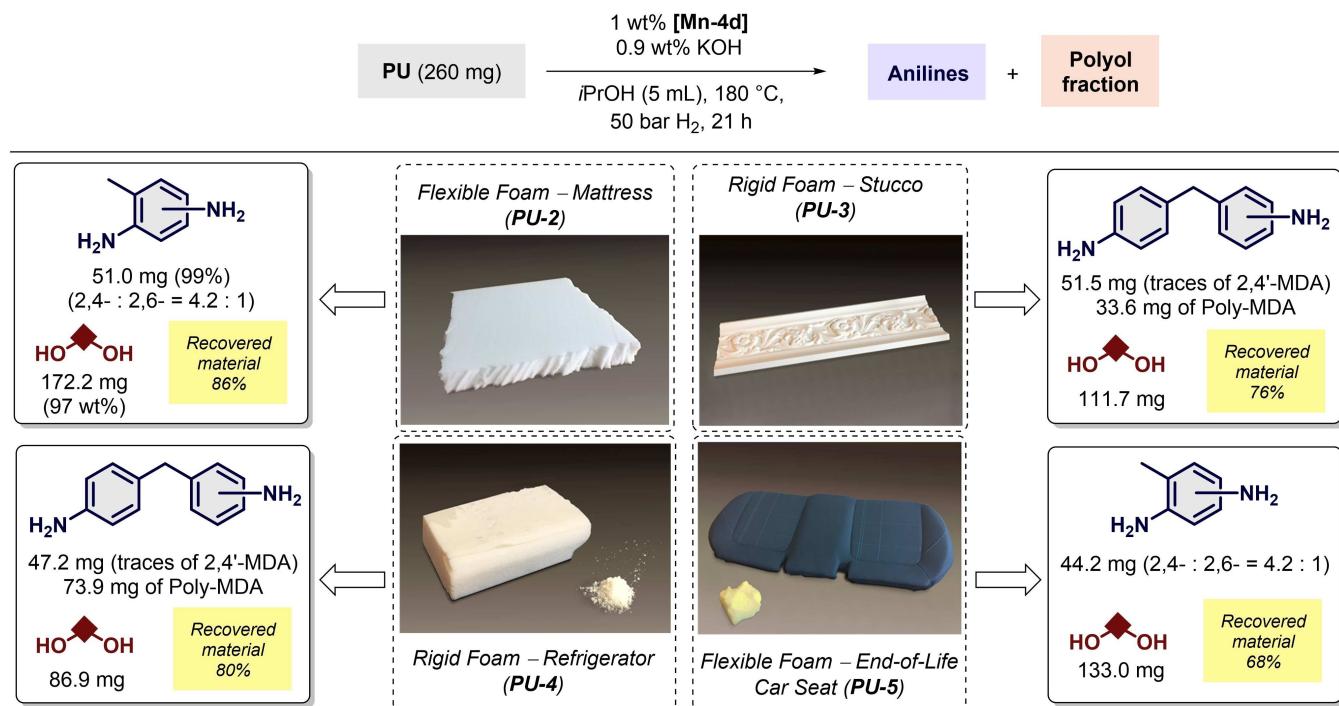


Figure 3. Catalytic hydrogenation of four commercial and end-of-life PU samples PU-2–PU-5 employing **Mn-4d**. All reactions were performed in a 45 mL autoclave fitted with a 30 mL poly(tetrafluoroethylene) inlay. Results are based on an average of two experiments. See the Supporting Information (Section 6d) for full details.

deconstructed in this mixture providing a 94% conversion to MDA and a 90% conversion to TDA (See the Supporting Information, Section 6d).

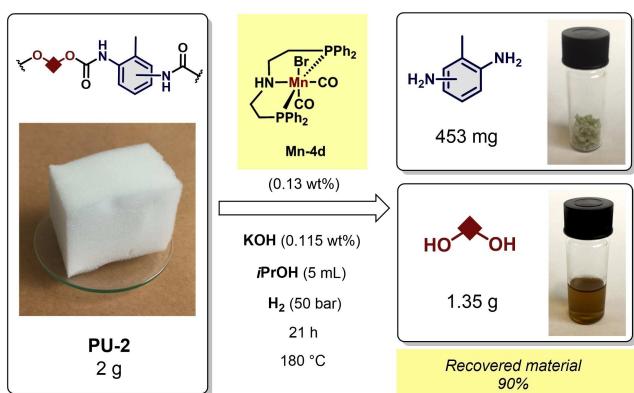
Next, a stucco (PU-3) was grinded down to fine particles, and 260 mg of this material was subjected to the optimized reaction conditions. This resulted in the isolation of an initial amine fraction and polyol fraction (the original composition of the polyurethane is unknown to us). On a closer inspection of the polyol fraction, a range of aromatic compounds were observed along with fire retardants. From a simple acid/base wash of the polyol fraction, 33.6 mg of polymeric MDA could be obtained, which to the best of our knowledge is the first time a polymeric MDA has been isolated following a catalytic deconstruction of polyurethane. Ultimately, this provided 85.1 mg of an aniline fraction and 111.7 mg of a polyol fraction, amounting to a 76% weight recovery.

The insulation material obtained from a refrigerator (PU-4) was also evaluated. As these materials are formed from a significant proportion of polymeric MDI, the same acid/base wash procedure as used for isolating the polyol fraction from hydrogenated PU-3 was adapted in the deconstruction of PU-4 for the isolation of polymeric MDA. After the catalytic hydrogenation of the refrigerator insulation material and an acid/base wash, 47.2 mg of an amine fraction of 4,4'-MDA (with traces of 2,4'-MDA) and 73.9 mg of polymeric MDA could be obtained along with 86.9 mg of the polyol fraction totaling an 80% mass recovery. Lastly, we tested the hydrogenative

deconstruction of PU-foam from an end-of-life car seat (PU-5) with **Mn-4d**. Satisfyingly, 44.2 mg of 2,4- and 2,6-TDA (4.2:1) along with 133 mg of polyol could be obtained, which amounts to a 68% material recovery. Moreover, from ³¹P-NMR of the polyol fraction, signals likely originating from a fire retardant were observed (see the Supporting Information, Section 8).

From here, the scalability of the reaction was evaluated (Scheme 2). Using PU-2, we could successfully increase the polymer loading to 2 g of sample, while keeping the catalyst loading to 2.6 mg (0.13 wt.%) and KOH loading to 2.3 mg (0.12 wt.%), without loss of any activity. More surprisingly, the amount of solvent could be kept to only 5 mL of isopropyl alcohol. Hence, a 1:2 weight ratio between the polymer and solvent could be used for the Mn-catalyzed deconstruction of flexible foam. Hereby, 453 mg of aniline and 1.35 g of polyol could be isolated, corresponding to a 90% of recovered material. Based on the isolated TDA, a TON of 905 could be calculated, which, compared to a TON of 970 for Schaub and co-worker's ruthenium complex^[26] and a TON of 62 for our previous Ir-based methodology,^[27] clearly shows the potential for using cheap abundant base metals for chemical recycling.

Lastly, a selection of experiments was devised to elucidate the possible mechanism of the Mn-catalyzed hydrogenative depolymerization of polyurethanes (see the Supporting Information, Section 6f). During this study, a range of formanilides were observed and isolated in cases of incomplete PU deconstruction. From this, it can be speculated that formani-



Scheme 2. Gram-scale Mn^{+2} MACHO-catalyzed hydrogenation of flexible foam (PU-2). The reaction was performed in a 45 mL autoclave fitted with a 30 mL poly(tetrafluoroethylene) inlay. See the Supporting Information (Sections 5 and 6e) for full details.

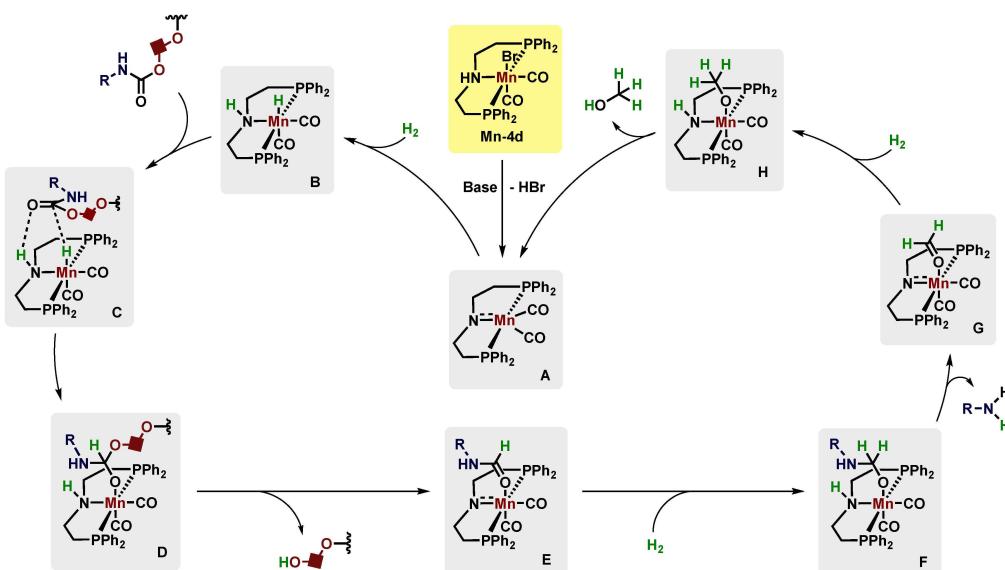
lides are intermediates formed during the hydrogenation of carbamates to anilines. To verify the viability of formanilides as intermediates, the corresponding formanilide of MDA was tested under the optimized reaction conditions resulting in 69% conversion to MDA (see the Supporting Information Section 6f). Moreover, the observed formation of MeOH could originate from the catalytic hydrogenation of formaldehyde. To investigate this, paraformaldehyde was tested as a substrate, which resulted in 81 % conversion to MeOH (see the Supporting Information, Section 6f). Based on these experiments and previous studies,^[32,48] a proposed catalytic cycle is presented in Scheme 3. Base activation of **Mn-4 d** forms the catalytic species **A**, which is subsequently reduced to the Mn complex **B** by the addition of dihydrogen to the $Mn=N$ double bond.^[32,48]

Subsequent interaction with the carbamate functionality (**C**), followed by Mn-hydride addition to the carbonyl group (**D**) and cleavage of the C–O bond leads to carbamate breakage, resulting in the formation of a free alcohol and the formanilide-ligated Mn complex **E**. The ensuing reduction of the formanilide and formaldehyde with dihydrogen proceeds in a similar fashion, passing through complexes **F**, **G**, and **H**.

Conclusion

In summary, we have reported on the first general manganese-based catalytic deconstruction of polyurethane. From an initial catalyst evaluation, it was found that the Mn^{+2} MACHO complex in combination with isopropyl alcohol, KOH and dihydrogen is effective for the catalytic hydrogenative depolymerization of real-life- and end-of-life PU samples. By utilizing this strategy, PU can be deconstructed to its monomeric components, from which virgin PU materials can be formed. The procedure was implemented on gram-scale, where flexible PU-foam was successfully deconstructed into aniline and polyol fractions with an overall 90% mass recovery. The transition from noble metals to base metals offers a clear advantage in terms of making PU recycling more cost-efficient. It is our expectation that the combination of green dihydrogen produced from electrolysis of water, in combination with inexpensive earth-abundant metals, can pave the way towards a circular plastic economy for PU.

During the preparation of this manuscript, Schaub and co-workers reported an alternative Mn catalyst for the catalytic hydrogenative deconstruction of commercial and end-of-life polyurethane materials,^[62] whereas Liu and Werner reported a transfer hydrogenation process for the reductive cleavage of simple linear polyurethanes with **Mn-4 d**.^[63]



Scheme 3. Proposed reaction pathway for the Mn-catalyzed hydrogenative deconstruction of carbamate-containing PU materials.

Supporting Information

Experimental details of the catalytic hydrogenations, catalyst synthesis, GC-MS data, and NMR spectral data are available in the Supporting Information.

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Conflict of Interest

The authors declare no conflict of interest.

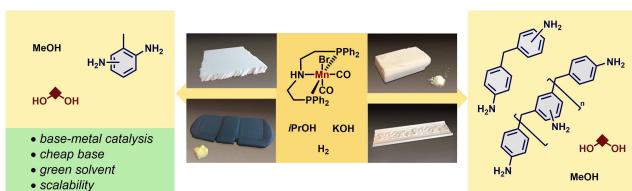
Keywords: homogeneous catalysis • hydrogenation • manganese • polymers • recycling

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Mn up the polyurethane recycling: A Mn pincer complex proves effective for the catalytic hydrogenation of polyurethane materials, providing the

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Evaluation of Manganese Catalysts for the Hydrogenative Deconstruction of Commercial and End-of-Life Polyurethane Samples

