Dioxomolybenum complex as an efficient and cheap catalyst for the reductive depolymerization of plastic waste into value-added compounds and fuels

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Abstract: This work describes the efficient and selective reductive depolymerization of PET, PBT, PCL, PLA and PDO plastic waste into value-added compounds and fuels, including 1,6-hexanediol, xylene and propane, catalyzed by the eco-friendly, cheap and air-stable dioxomolybdenum complex $MoO_2Cl_2(H_2O)_2$ using silanes as reducing agents. The catalyst $MoO_2Cl_2(H_2O)_2$ can be used in at least 8 catalytic cycles in the reductive depolymerization of PCL with excellent activity and the catalytic system $PMHS/MoO_2Cl_2(H_2O)_2$ was successfully applied in the production of propane from the reductive depolymerization of PLA on gram scale. Moreover, this method was also efficiently applied in the selective reduction of a PCL, PLA and PET mixture.

Keywords: plastics, polyesters, reductive depolymerization, dioxomolybdenum complex, silanes.

Introduction

Plastic plays an important role in improving our lifestyles in numerous sectors such as healthcare, construction, packaging, electronic, automotive, etc, and living without plastics is almost impossible. In fact, this material has some excellent properties such as low density, high mechanical strength, impermeability to water and low cost, among others, that makes it very useful. However, it is estimated that only 9% of all plastics ever produced have been recycled and that about 79% were accumulated in landfills or in the environment.[1] As a consequence, plastics are increasingly problematic from an environmental and sustainability perspective.

In this context, the development of selective depolymerization methods that can be used to break down waste polymers into valuable monomers or chemicals appears a promising strategy and also as an emerging research area.[2-4] From the point of view of energy conservation and environmental protection, plastic waste is among the

most valuable waste materials and can be regarded as a potentially cheap source for the production of fuels and chemicals for industry.

In the literature there are described only few methods for the reductive depolymerization of polyesters. For example, different ruthenium complexes have been used as catalysts for the hydrogenative depolymerization of polyesters into diols.[5-7] Cantat and coworkers[8,9] investigated the reductive depolymerization of plastic waste using silanes as reducing agents. Initially, these authors employed the commercially available $B(C_6F_5)_3$ and $[Ph_3C^+,B(C_6F_5)_4^-]$ catalysts[8] and more recently, this research group reported the reductive depolymerization of plastic waste catalyzed by the iridium complex $[Ir(PCP)H(THF)][B(C_6F_5)_4]$ (PCP = $1,3-(t-Bu_2P)_2C_6H_3$), obtaining the corresponding silyl ethers or alkanes, depending only on the reaction temperature.[9] However, one of the disadvantages of these methods is the price of catalysts, which is an obstacle for a scale-up process development, and the search for efficient, economical, environmentally friendly, and reusable catalysts for the reductive depolymerization of plastic waste to value-added compounds and fuels remains highly desirable for the sustainability of the planet.

Dioxomolybdenum complexes have been used as excellent catalysts for the reduction or deoxygenation of a wide variety of organic compounds[10,11,12]. These results have encouraged us to investigate the use of an high-valence oxo-molybdenum complex as catalyst for the reductive depolymerization of plastic waste.

In this work, we will study the reductive depolymerization of real plastic waste into value-added compounds and fuels using silanes as reducing agents catalyzed by $MoO_2Cl_2(H_2O)_2$, a cheap and air-stable catalyst, with an easy and inexpensive preparation, obtained only by extraction from a hydrochloric acid solution of Na_2MoO_4 with diethyl ether.[13]

Results and discussion

Polycaprolactone (PCL) is a synthetic aliphatic polyester obtained from ring-opening polymerization of caprolactone, a cyclic carboxylic ester that is often derived from fossil carbon.[14] In this work, we initially studied the reductive depolymerization of a granulated PCL sample catalyzed by $MoO_2Cl_2(H_2O)_2$ using different silanes as reducing agents (Table 1). The reaction with the reducing agent polymethylhydrosiloxane (PMHS, 2 equiv.), a byproduct of the silicone industry, cheap, easy to handle, and environmentally friendly, was carried out using 2 mol% of

MoO$_2$Cl$_2$(H$_2$O)$_2$ in toluene at 110 ºC, leading to a 95% conversion of PCL and a 84% yield of 1,6-hexanediol (Table 1, entry 1). The formation of 1,6-hexanediol was confirmed by the analysis of ^{1}H NMR spectrum and an ESI full scan mass spectrum. 1,6-Hexanediol is an important value-added compound as a result of its increasing number of applications in different industries, such as polyurethanes, coatings, adhesives, acrylates, unsaturated polyester resins, plasticizers and others.[15-21] This methodology has the advantage of directly giving 1,6-hexanediol from PCL without the need to carry out the hydrolysis of silyl ethers.

The best result was obtained with 1 mol% of this catalyst and 1.5 equiv. of PhSiH$_3$ after 20 h in toluene at 110ºC, leading to the complete reduction of PCL with formation of 1,6-hexanediol in 85% yield (Table 1, entry 2). The effect of the temperature was also evaluated in the reductive depolymerization of PCL using 1 mol% of MoO$_2$Cl$_2$(H$_2$O)$_2$ and 1.5 equiv. of PhSiH$_3$. At 80 ºC, PCL was converted in 95% after 24 h (Table 1, entry 3), but at room temperature this reduction did not occur, even after 48 h (Table 1, entry 4). The reductive depolymerization of PCL was also tested using THF as solvent, however, only a 75% PCL conversion and 63% 1,6-hexanediol yield were obtained (Table 1, entry 5).

Table 1 – Reductive depolymerization of PCL using different silanes[a]

Entry	MoO$_2$Cl$_2$(H$_2$O)$_2$ (mol%)	Silane	Silane (equiv.)	Solvent	Temp. (ºC)	Time (h)	Conversion (%)	Product (%)[b]
1	2	PMHS	2	Toluene	110	48	95	84
2	1	PhSiH$_3$	1.5	Toluene	110	20	100	85
3	1	PhSiH$_3$	1.5	Toluene	80	24	95	81
4	1	PhSiH$_3$	1.5	Toluene	r. t.	48	No reaction	–
5	1	PhSiH$_3$	1.5	THF	110	24	75	69 (25)[c]
6	5	DMPS	3	Toluene	110	24	80	78 (20)[c]
7	5	Pr$_3$SiH	3	Toluene	110	48	No reaction	–
8	5	Et$_3$SiH	3	Toluene	110	48	No reaction	–
9	5	Ph$_3$SiH	3	Toluene	110	48	No reaction	–
10	5	–	–	Toluene	110	48	No reaction	–
11	–	PhSiH$_3$	2	Toluene	110	48	No reaction	–

[a]The reactions were carried out with 0.5 mmol of PCL. [b]Yields were determined by ^{1}H NMR spectroscopy using mesitylene as internal standard. [c]PCL yield.

Dimethylphenylsilane (DMPS, 3 equiv.) was also applied as reducing agent in this reaction in the presence of 5 mol% of $MoO_2Cl_2(H_2O)_2$, producing 78% of 1,6-hexanediol, along with 20% of PCL after 24 h (Table 1, entry 6). In contrast, the reductive depolymerization of PCL did not occur with the silanes Et_3SiH, Pr_3SiH and Ph_3SiH after 48 h, even using higher amounts of silane (3 equiv.) and $MoO_2Cl_2(H_2O)_2$ (5 mol%) (Table 1, entries 7-9). Finally, no reaction was observed in the absence of silane or catalyst (Table 1, entries 10 and 11).

In this work, we also explored the possible use of the catalyst $MoO_2Cl_2(H_2O)_2$ in multiple cycles in the reductive depolymerization of PCL in toluene at 110 ºC by successive additions of PCL and $PhSiH_3$ to the reaction mixture, without separating the catalyst at the end of each cycle. The yield of each catalytic cycle was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard. We found that the catalyst can be used in at least 8 cycles with excellent activity. In the first three cycles, the total conversion of PCL occurred and in the cycles 4-8, a PCL conversion of 95% was observed.

To confirm if 1,6-hexanediol is reduced with the catalytic system silane/$MoO_2Cl_2(H_2O)_2$, we carried out the reaction of 1,6-hexanediol with 1 mol% of $MoO_2Cl_2(H_2O)_2$ and 2 equiv. of PMHS in toluene at 110 ºC during 48 h and we found that 1,6-hexanediol did not react under these reaction conditions.

Polylactic acid (PLA) is a linear, aliphatic polyester that derives from renewable resources such as corn, sugarcane, potato starch or tapioca and can be an alternative to petroleum derived polymers. This polyester is biocompatible and has been applied in the biomedical field as wound closures, tissue scaffolds, drug delivery systems, bone surgery and implants.[22] PLA is also used in food packaging, bags, disposable tableware, upholstery, disposable garments, hygiene products and even diapers. Additionally, the ease with which PLA melts allows for some interesting applications in 3D printing, including in the production of complex biomedical devices according to computer design using patient-specific anatomical data as well as in wide range of industrial and architectural applications.

The reductive depolymerization of polyester PLA, obtained from a beverage cup cut into pieces, was investigated using PMHS (2 equiv.) as reducing agent in the presence of 2 mol% of $MoO_2Cl_2(H_2O)_2$ in toluene at 110 ºC during 40 h (Table 2, entry 1). Interestingly, the analysis of the ^{1}H NMR spectrum of the reaction mixture showed

95% conversion of PLA, however, the signals of the expected product 1,2-propanediol were not observed. This result suggests the formation of propane, whose signals were observed in the ^{1}H NMR spectrum after 20 h. The formation of propane was also confirmed by GC. Due to the high volatility of propane, this product was not detected in the solution at the end of the reaction and its yield could not be determined.

The reduction of PLA was also performed with PhSiH$_3$ (1.5 equiv.) and MoO$_2$Cl$_2$(H$_2$O)$_2$ (1 mol%) in toluene at 110 ℃ during 20 h, leading to the full conversion of PLA with formation of propane (Table 2, entry 2).

Table 2 – Reductive depolymerization of PLA using different silanes[a]
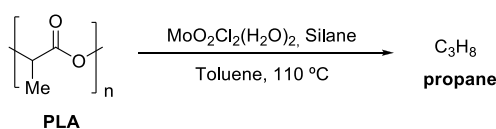
| Entry	MoO$_2$Cl$_2$(H$_2$O)$_2$ (mol%)	Silane	Silane (equiv)	Time (h)	Conversion (%)[b]
1	2	PMHS	2	40	95
2	1	PhSiH$_3$	1.5	20	100

[a]The reactions were carried out with 0.5 mmol of PLA. [b]The conversions were determined by ^{1}H NMR using mesitylene as internal standard.

Then, we studied the reaction of 1,2-propanediol with MoO$_2$Cl$_2$(H$_2$O)$_2$ (1 mol%) and PhSiH$_3$ (1.5 equiv.) in toluene at 110 ℃ in order to see if this diol is reduced to propane under the same reaction conditions. The analysis of the ^{1}H NMR spectrum of the reaction mixture after 30 h showed that 1,2-propanediol was complete consumed, also suggesting the formation of propane.

We also decided to test this reaction in the reductive depolymerization of PLA obtained from 3D printer waste using MoO$_2$Cl$_2$(H$_2$O)$_2$ (2 mol%) and PhSiH$_3$ (2 equiv.) in toluene at 110 ℃ during 30 h, observing the complete conversion of PLA. This result demonstrated that the presence of pigments in these wastes did not affect the efficiency of the reaction. The successfully application of this reaction in the valorization of 3D printer waste is also interesting, since nowadays 3D printing is used for a large range of applications in industries such as architecture, civil and general engineering, industrial design, aerospace, construction, automotive engineering and also in medical industry.

To evaluate the possible scale-up of this methodology, the reductive depolymerization of a PLA beverage cup, cut into pieces, was performed on a gram scale using PMHS as reducing agent, leading to a 86% conversion of PLA into propane after 4 days. This result is very interesting because it shows the possible application of this cheap and environmentally friendly catalytic system to the large scale production of propane from PLA, a polyester derived from renewable resources, contributing to reduce its production from fossil sources.

Poly(dioxanone) (PDO) is a synthetic polymer of multiple repeating ether-ester units, prepared by ring-opening polymerization from the monomer p-dioxanone.[23] The reaction of a granulated PDO sample with $MoO_2Cl_2(H_2O)_2$ (2 mol%) and $PhSiH_3$ (2 equiv.) in chlorobenzene at 110 ℃ led to the full reduction of this polymer after 20 h (Eq. 3). The ^{1}H NMR spectrum of the reaction mixture showed only the formation of a very small amount of ethylene glycol (12%), suggesting the conversion of this compound into ethane (Scheme 1), as observed in another methodology.[9]
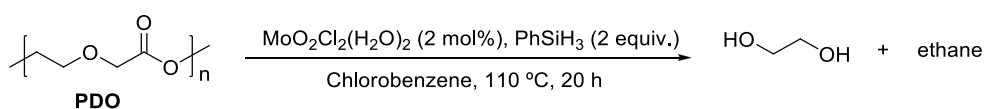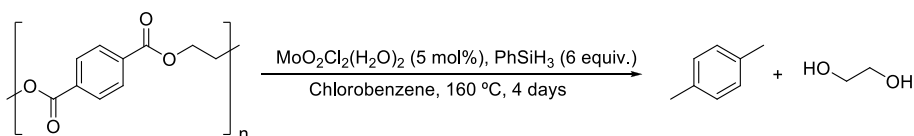

Scheme 1 – Reductive depolymerization of PDO with the catalytic system $MoO_2Cl_2(H_2O)_2$/$PhSiH_3$.

With aim to explore the applicability of this methodology for the valorization of hospital waste and medical plastic materials, we also tested the reductive depolymerization of PDO surgical suture catalyzed by $MoO_2Cl_2(H_2O)_2$ (2 mol%) using $PhSiH_3$ (2 equiv.) in chlorobenzene at 110 ℃. After 20 h, the ^{1}H NMR spectrum of the reaction mixture confirmed that all surgical suture was reduced with formation of a small amount of ethylene glycol (11%) in agreement with the result obtained in the reductive depolymerization of the granulated PDO sample. Although plastic cups, forks or containers can be washed and reused, several orthopedic or hospital plastic materials cannot be reused, and this method can be used to convert medical supply waste into value-added products.

Polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) are two very useful polyesters with a wide range of applications in our life. For example, due to its exceptional durability, thermal and rheological properties, PET, the most common polyester, is used in food and beverage packaging material (mainly, water

bottles and soft-drink bottles), houseware, electronics, automotive parts, sports goods, and textiles.

The reductive depolymerization of PET required harsher reaction conditions than PCL, PLA or PDO, probably due to the low solubility of this polymer. The reaction was performed with PET obtained from a commercial Evian[©] water bottle finely ground, using 5 mol% of $MoO_2Cl_2(H_2O)_2$ and an excess of $PhSiH_3$ (6 equiv.) in chlorobenzene at 160 °C. After 4 days, the ^{1}H NMR spectrum of the reaction mixture showed the formation of xylene in 65% yield, along with ethylene glycol (Scheme 2). No signals corresponding to PET were observed, demonstrating that all solubilized PET was reduced. However, small pieces of insoluble PET were visible at the end of the reaction. The signals of the intermediate 1,4-benzenedimethanol were also not visible in the ^{1}H NMR spectrum at the end of the reaction.
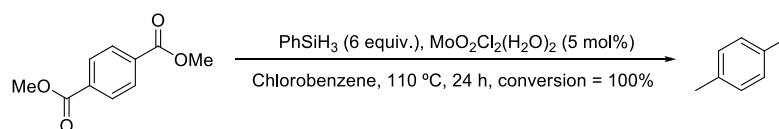

Scheme 2 – Reductive depolymerization of PET with the catalytic system $MoO_2Cl_2(H_2O)_2/PhSiH_3$.

When the reaction mixture was heated for a prolonged reaction time (7 days at 160 °C), the signals of ethyl glycol disappeared in the ^{1}H NMR spectrum, suggesting the reduction of this diol to ethane.

To evaluate the general applicability of this new methodology, these reaction conditions were also successfully applied to the reductive depolymerization of PET obtained from other sources, including a synthetic pillow filling or a sport jersey, leading to the formation of xylene with 62-65% yields, respectively. The reduction efficiency was not affected by the presence of additives and pigments in the different PET samples. As polyester is the most popular fabric used in fashion, this method can also help solve the problem associated with the increasing impact of textile waste on the environment.

To confirm the reductive deoxygenation of ester groups to methyl groups during the xylene formation, the reduction of dimethyl terephthalate catalyzed by $MoO_2Cl_2(H_2O)_2$ using phenylsilane as reducing agent was performed in chlorobenzene at 110 °C (Scheme 3). After 24 h, the ^{1}H NMR spectrum of the reaction mixture showed the full reduction of dimethyl terephthalate with the formation of xylene, confirming the

efficiency of the catalytic system silane/$MoO_2Cl_2(H_2O)_2$ for the reductive deoxygenation of ester groups. This result also proves that the low solubility of PET limits the efficiency of its reductive depolymerization, as the dimethyl terephthalate monomer can be completely reduced in only 24 h at 110 ºC, in contrast to the 4 days at 160 ºC required for the partial reduction of PET.

Scheme 3 – Reduction of dimethyl terephthalate with the catalytic system $MoO_2Cl_2(H_2O)_2$/$PhSiH_3$.

The reductive depolymerization of a granulated PBT sample was also tested using the same reaction conditions described for the reaction of PET (Scheme 4). The ^{1}H NMR spectrum of the reaction mixture after 4 days showed the full reduction of PBT with the formation of xylene in 86% yield.
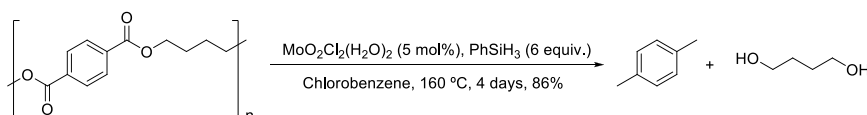
Scheme 4 – Reductive depolymerization of PBT with the catalytic system $MoO_2Cl_2(H_2O)_2$/$PhSiH_3$.

These reaction conditions were also applied to the reductive depolymerization of a PBT sample obtained from an engine component (distributor cap) of a car, leading to the formation of xylene.

Considering that most plastic waste in landfills and municipal solid waste are composed of a mixture of different polymers, it is also very interesting to investigate the reductive depolymerization of a plastic mixture. In this context, we performed the reductive depolymerization of a PCL, PLA and PET mixture using $MoO_2Cl_2(H_2O)_2$ and PMHS in chlorobenzene at 110 ° C for 48 h. The ^{1}H NMR spectrum of the reaction mixture showed complete conversion of PCL to 1,6-hexanediol. The signals of PLA were not visible in the spectrum, also suggesting the total reduction of this polymer into gas propane. Finally, the spectrum showed no signs corresponding to the formation of any product from PET, demonstrating that under these conditions PET did not react, becoming insoluble in solution. This reaction can contribute to the treatment and valorization of complex polymer mixtures, leading to the separate production of 1,6-

hexanediol, which remains in solution, propane gas and insoluble PET, which can be removed by filtration and reduced separately.

Conclusion

We report a novel methodology for the reductive depolymerizaion of several real plastic waste using the oxo-molybdenum complex $MoO_2Cl_2(H_2O)_2$ as a very efficient, cheap and environmentally friendly catalyst. This is the first reductive depolymerization of plastic waste using a molybdenum catalyst. Another important advantage of this process includes the use of PMHS as an environmentally benign, inexpensive, non-toxic and air and moisture stable reducing agent. Other advantages of this methodology are the use of the catalyst $MoO_2Cl_2(H_2O)_2$ in at least 8 catalytic cycles and on gram scale. Together, all these advantages make this catalytic protocol a green and highly economical process for the reductive depolymerization of plastic waste with potential to be utilized in the industrial scale**.**

The application of this methodology to the production of propane from PLA, a polyester derived from renewable resources, can contribute to reduce its production from fossil sources. Further studies on the use of other homogeneous and heterogeneous oxo-molybdenum catalysts for the reductive depolymerization of plastic waste are ongoing in our group.

Finally, we demonstrated that this methodology can be efficiently applied to the reductive depolymerization of a variety of real plastic waste obtained from domestic waste or generated from different industries including textile, hospital, electronics, or automobile, contributing to solve the two most concerned issues that the planet is facing nowadays related with energy and environment.

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