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Recycling of Rare Earth Elements: From E-Waste to Stereoselective Catalytic Reactions

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

Abstract: Raw mixtures of Rare Earths Elements, REE, recovered by E-waste, were used as catalysts to promote the (stereoselective) synthesis of highly valuable compounds. Y_2O_3 , the major species that is recovered by the E-waste, can be easily converted into the catalytically active $Y(OTf)_3$ that is able to efficiently promote the Michael addition of indoles to benzylidene malonates and the stereoselective Diels-Alder cycloaddition between cyclopentadiene and 4-(S)-3 acryloyl 4-tert-butyl 2-oxazolidinone. Additionally, the raw mixtures were immobilized onto silica and used to construct packed reactors, resulting in values for Productivity and Space-Time Yields that were significantly higher than those of the corresponding batch conversions. Notably, the prepared cartridge employed in the model Michael reaction maintained its catalytic efficiency for more than 4 days of continuous running.

Introduction

The EU regards the circular economy paradigm as particularly relevant for the “critical raw materials” (CRM).^[1] Given their importance for high-tech industries and the concentration of world supply, Rare Earths Elements (REE) are the utmost critical for the EU economy, and, among others, are listed as critical raw materials. REE become a critical commodity also because of their growing demand and their small and opaque market.^[2-3] In order to secure world's RE demand for the future and to reduce their supply risk, most researchers focused on the development of recycling processes, looking at the electronic waste as starting material.

E-waste management has become one of the most critical areas for waste management policies.^[4] Many groups are dealing with RE recovery from magnets or fluorescent lamps, because they

represent 68% of these metals used in terms of economic value.^[5] However, despite the large number of studies, the recovery of REE from electrical and electronic equipment waste (WEEE) is not conducted, in the most cases, at industrial scale. Main reasons are the low technology readiness level and the heterogeneous waste streams and qualities of these WEEE.

The recycling processes depicted in the literature are focused on RE recovery from WEEE to be re-used in the same application, requiring a complex purification of these metals and contributing in many ways to uneconomical processes.^[6]

In this regard, the present study offers another perspective in the framework of the REE recycling. From WEEE, the recovered REEs will be reused as reagents in a new chemical application. The aim of this study is to demonstrate that raw mixtures of REE recovered by E-waste, can be used as catalysts able to promote the synthesis of highly valuable compounds. That would represent an innovative and outstanding recycling of REE, by avoiding the required steps and expenses necessary for the reuse of REE in electronic industry, and enhancing the value of raw materials, employed in a totally different field, as key players for the synthesis of highly functionalized (chiral) molecules, including biologically active compounds.

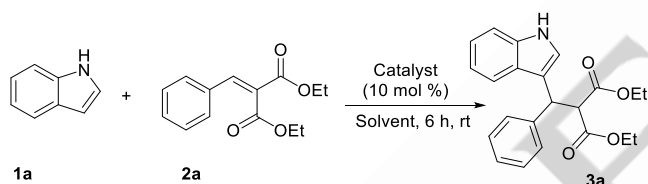
In our preliminary study, we have focused on Yttrium, that is listed as CRM in the group of heavy rare earths.^[7] Two different raw mixtures, recovered from fluorescent lamps, after treatment with trifluoromethanesulfonic acid to convert the elements in triflate salts, were successfully employed to promote two different reactions, a Michael addition and a stereoselective Diels-Alder cycloaddition (please see the Supporting Information for details about sources of raw materials. We thank FNE Entsorgungsdienste Freiberg, Germany for providing the samples

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of EoL-Waste). Furthermore, the raw mixtures, containing Yttrium with many other elements, were immobilized on silica; the supported catalytic species were able to promote in high yields the reactions in batch, and could be recycled five times. Finally, the silica-supported catalyst was used to prepare a packed bed reactor that was successfully used to efficiently perform the organic reactions under continuous flow conditions, with very high productivity.

Results and discussion

Y_2O_3 is the major species that is recovered by the E-waste, but typically it is not catalytically active. However, it can be easily converted into $Y(OTf)_3$, a widely used catalyst for several transformations, according to a literature protocol, by reacting Yttrium oxide with trifluoromethanesulfonic acid.^[8] At the beginning of our investigation, the Michael addition of indole **1a** to benzylidene malonate **2a** was selected as model reaction (Scheme 1). As expected, the reaction is not promoted by Y_2O_3 , (entry 1, Table 1), or by CF_3SO_3H that leads to extensive reagent decomposition, but it is efficiently catalysed by $Y(OTf)_3$. For sake of comparison the behaviour of commercially available yttrium triflate as catalyst for this transformation was studied, under different experimental conditions and solvents (Table 1).



Scheme 1. Model reaction: Michael addition of indole **1a** to benzylidene diethyl malonate **2a** to afford product **3a**.

Table 1. Yttrium-catalysed addition of indole to benzylidene diethyl malonate.

Entry ^[a]	Catalyst	Solvent	Yield (%) ^[b]
1	10% Y_2O_3	Et_2O	-
2	1% CF_3SO_3H	CH_3CN	-
3	10% $Y(OTf)_3$	Et_2O	85
4	10% $Y(OTf)_3$	CH_3CN	73
5	10% $Y(OTf)_3$	Cyclopentyl methylether	45
6	10% $Y(OTf)_3$	MeOH	81
7	10% $Y(OTf)_3$ + 5% $CoCl_2 \cdot 6 H_2O$	MeOH	64
8	10% $Y(OTf)_3$ + 10% $CoCl_2 \cdot 6 H_2O$	MeOH	64
9	10% $Y(OTf)_3$ + 5% $SmCl_3$	MeOH	65
10	10% $SmCl_3$	MeOH	22
11	10% $CoCl_2 \cdot 6 H_2O$	MeOH	-

^[a] Reaction performed at RT for 6 hours, ^[b] Determined by 1H NMR and confirmed as isolated yield after chromatographic purification.

Among the different tested solvents, diethyl ether and methanol led to better results, but the reaction worked well also in acetonitrile and in the green solvent cyclopentyl methyl ether (entries 3-7). In order to mimic the behaviour of the REE mixtures recovered from E-waste, where Y is present in combination with other metals, different Lewis acids were added as impurities to the commercial $Y(OTf)_3$. As shown in Table 1, the reaction works in the presence either of $SmCl_3$ or $CoCl_2$, while, noteworthy, both Sm and Co species alone are not good catalysts (see the Supporting Information for complete screening details). Homemade Yttrium triflate was prepared by treating yttrium oxide with trifluoromethanesulfonic acid, filtered and dried under vacuum, and it was compared to the commercially available $Y(OTf)_3$. The material proved to be able to promote the reaction, although in slightly lower yields, possibly due to hydration of the catalyst and/or uncomplete Y_2O_3 conversion (see the supporting information for further details and kinetic data).

After these preliminary studies, two samples of electronic waste were examined for their catalytic activity in the Michael addition. Two fluorescent lamp scrap samples, classified as (RM1) and (RM2), were used (Figure 1).^[9] Both samples were of commercial end-of-life (EoL) material from spent fluorescent lamps. The slurry was dried to weight constancy and subjected to solid state chlorination (SSC) using ammonium chloride to produce gaseous hydrochloric acid from which the rare earth elements (REE) were yielded as their chlorides. After suspending and dissolution in water, the REE were precipitated as their oxalates to give a mixed rare earth oxalate which after calcination at 1,000°C in a muffle furnace gave the oxides with Y_2O_3 as the major component of interest.

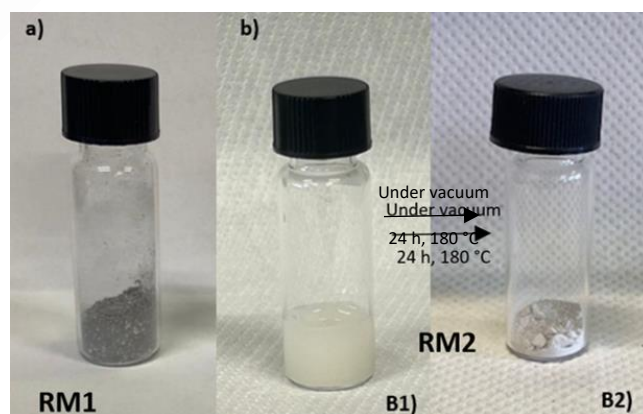


Figure 1. a) Raw mixture recovered from fluorescent lamps (RM1). b) Raw mixture recovered from fluorescent lamps (RM2), as aqueous suspension (B1) and after drying under vacuum for 24 h at 180 °C (B2).

ICP-MS analysis was performed on both samples. The results of the analysis are reported in the Table 2 and show that Y was detected as 13% in both samples. XRPD analysis of the RM1 was

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also done and evidenced the presence of Y_2O_3 , while in the XPS analysis, the presence of different metals was observed (Co, Zn, Er, Y, Na and Al, for further details and spectra see the Supporting Information).

Table 2. ICP-MS analysis on some components of raw mixtures recovered from E-Waste.

Raw mixture	Pr (%)	Eu (%)	Y (%)	La (%)	V (%)
RM1 (oxide)	0.13	0.94	13.07	/	/
RM2 (oxide)	0.26	0.23	12.70	1.73	1.24

The addition of indole to benzylidene diethyl malonate in the presence of both the raw mixtures (RM1 and RM2) did not afford any product, as expected, since mostly the catalytically inactive Yttrium oxides were present in the recovered mixtures. After treatment of RM1 and RM2 with trifluoromethanesulfonic acid, the triflate derivatives of RM1 and RM2 (RM1-OTf and RM2-OTf), were indeed able to efficiently promote the reaction, with comparable yields (entries 4-7, Table 3). In particular, RM2-OTf was especially efficient in catalysing the Michael addition even with low Yttrium loading, in yields higher than 80% after 6 hours (entries 9 and 11, Table 3 compared to 10% of commercial $Y(OTf)_3$, entries 1 and 2, Table 3). Moreover, it is possible to notice that the RM2-OTf is catalytically more active compared to the RM1-OTf.

Table 3. Indole addition to benzylidene diethyl malonate catalysed by recovered mixtures from E-waste, RM1 and RM2.

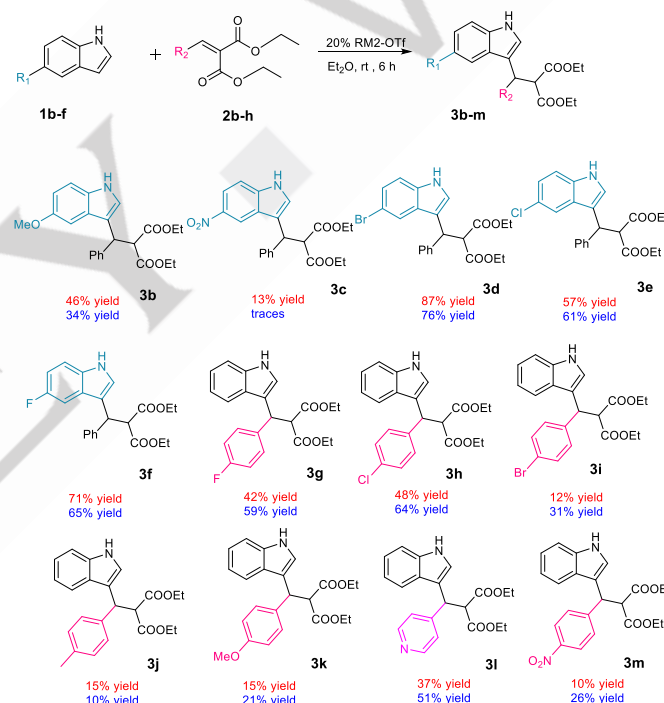
Entry[a]	Catalyst	Y loading (%)	Solvent	Yield (%) [b]
1	10% $Y(OTf)_3$ comm.	10%	MeOH	81
2	10% $Y(OTf)_3$ comm.	10%	Et ₂ O	85
3	RM1-OTf (20%)	2.4%	MeOH	57
4	RM1-OTf (20%)	2.4%	Et ₂ O	52
5	RM1-OTf (40%)	4.8%	MeOH	64
6	RM1-OTf (40%)	4.8%	Et ₂ O	66
7	RM2-OTf (10%)	0.9%	Et ₂ O	43
8	RM2-OTf 20%)	1.8%	MeOH	74
9	RM2-OTf (20%)	1.8%	Et ₂ O	80
10	RM2-OTf (40%)	3.7%	MeOH	86
11	RM2-OTf (40%)	3.7%	Et ₂ O	91

[a] Reaction performed at RT for 6 hours [b] Determined by 1H NMR and confirmed as isolated yield after chromatographic purification.

The more catalytically active RM2-OTf was then used to investigate the scope of the reaction and the applicability of such metal mixtures in the synthesis of differently functionalized

substrates. Therefore, the reaction between indoles 1b-f and benzylidene diethyl malonates 2b-h was performed for 6 hours at room temperature in diethyl ether. In Scheme 2 yields obtained using RM2-OTf as catalyst (1.8 % of Yttrium loading) are reported in blue, while in red, for sake of comparison, the yields of the reaction catalysed by pure $Y(OTf)_3$ are reported.

The presence of halogens in 5 position of indoles is well tolerated and the products were isolated in satisfactory yields. The reaction of 5-methoxy indole gave the adduct 3i in lower yield, while only traces of the product were observed with 5-nitroindole 1c. The addition of indoles to differently substituted benzylidene malonates (2b-2h) led the products in moderate to good yields. However, it is worth mentioning that with all the studied derivatives, RM2-OTf activity was comparable to that of commercial $Y(OTf)_3$.

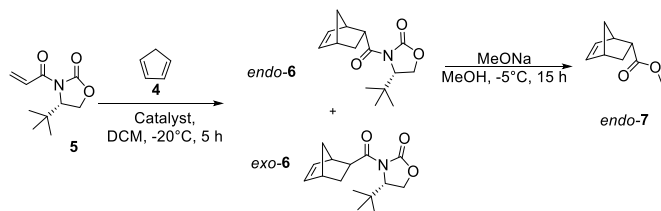


Scheme 2. Scope of the Michael addition catalysed by RM2 triflate.

To further demonstrate the versatility and the general applicability of the recovered raw mixture in different reactions, a more challenging transformation was studied. The stereoselective Diels-Alder cycloaddition between cyclopentadiene 4 and 4-(S)-3 acryloyl 4-tert-butyl 2-oxazolidinone 5 was investigated (Scheme 3).^[10] The reaction was run at -20°C for 5 hours, to afford the product 6 as mixture of the *endo* and the *exo* isomers. The crude was purified by a filtration on a short pad of silica gel, and the diastereoisomeric ratio was evaluated by 1H -NMR. Then the crude was reacted with MeONa in MeOH to remove the chiral auxiliary and to afford product 7, as mixture of enantiomers, and the enantiomeric excess could be determined by HPLC on chiral

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stationary phase. The results are shown in Table 4, where in entry 1 for sake of comparison the data obtained with pure yttrium triflate are included.



Scheme 3. Stereoselective Diels-Alder cycloaddition catalysed by RM1 and RM2 triflates.

Table 4. Diels-Alder cycloaddition catalysed by RM1 and RM2 triflates. ^[a]

Entry	Catalyst	Y Loading (%)	Yield ^[b] (%)	Endo /exo ^[c]	e.e. endo ^[d] (%)
1	10% Y(OTf) ₃	10	86	81/19	96
2	RM1-OTf (10%)	1.2	57	80/20	87
3	RM2-OTf (10%)	0.9	90	86/14	91

^[a] Reaction performed at -20°C for 5 hours ^[b] Isolated yield ^[c] Determined by ¹H NMR and confirmed as isolated yield after chromatographic purification ^[d] Determined by HPLC on chiral stationary phase.

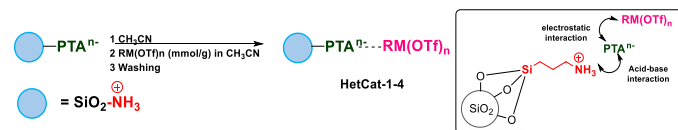
Moreover, the raw mixture triflate RM2, was able to promote the reaction with a 10% loading of the mixture, corresponding to only 0.9% loading of Yttrium in 90% yield, 86/14 diastereoisomeric ratio and 91% e.e. of the major *endo* isomer (entry 3, Table 4).

The possibility to use the recovered raw mixtures from E-waste was demonstrated, in different reactions, including a stereoselective transformation where comparable levels of chemical and stereochemical yields with pure Y(OTf)₃ were reached. However, when the recycle of those catalytic mixtures was attempted, poor reproducibility was observed. Therefore, we turned our attention to the opportunity offered by the catalyst immobilization.^[11]

Based on the seminal work by Kobayashi and co-workers, which described the synthesis of a chiral Sc(III) catalyst anchored by an acid-base interaction to a functionalised silica with amino triethoxysilane and heteropoly acid,^[12] the immobilisation of the heterogeneous triflates mixtures, RM1-OTf and RM2-OTf, was studied, following an experimental procedure recently reported by our group.^[13] The recovered mixtures, RM1 and RM2, were converted into the triflates derivatives, by using different amounts of trifluoromethanesulphonic acid. The RM triflates were then reacted with the functionalised silica materials (Scheme 4) to afford different materials, as reported in Table 5.

The immobilization efficiencies were evaluated on the washed-out yttrium according to the published procedure.^[13] Moreover, TEM

and EDX analysis were performed on the best catalyst, HetCat-4-RM2. The analyses are reported in the supporting information.



Scheme 4. Synthesis of immobilized RM-Triflates on functionalised silica

Table 5. Immobilization efficiency and effective catalyst loading of supported catalyst using raw mixture.

Entry	Catalyst	CF ₃ SO ₃ H (equiv.)	Imm. efficiency (%)	Y supported (mmol/g)
1	HetCat-1-RM1	6	65	0.065
2	HetCat-2-RM1	12	76	0.076
3	HetCat-3-RM2	6	92	0.092
4	HetCat-4-RM2	12	96	0.096

After the synthesis of the supported catalysts, they were tested in the Michael addition in different solvent, obtaining moderate to good results in different solvents. The HetCat-4-RM2 showed the best performance (Table 6).

Table 6. Michael addition of indole **1a** to benzylidene diethyl malonate **2a** using supported raw mixtures

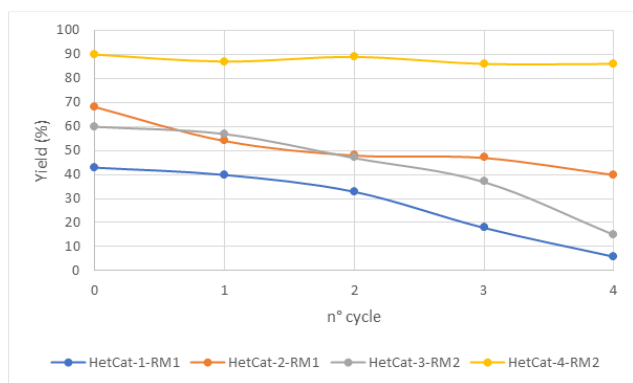
Entry	Catalyst	Catalyst loading (%)	Yield (%) (in MeOH)	Yield (%) (in CH ₃ CN)
1	Hetcat-1-RM1	12	41	43
2	Hetcat-2-RM1	15	54	51
3	Hetcat-3-RM2	14	61	60
4	Hetcat-4-RM2	14	78	90

Moreover, all the catalysts were successfully recycled. The HetCat-4-RM2 gave very good results compared to the other catalysts after four recycles. The recycling reactions were conducted using CH₃CN as a solvent since it is the best solvent for this transformation. Leaching tests showed that in methanol some Y leaching was detected, while in acetonitrile HetCat-4-RM2 showed a very limited leaching, which was confirmed by the ICP-OES of the solution, where 3.38 ppm of Y were detected. **§§** Using CH₃CN as the solvent of choice, the recycling tests were performed using all the supported catalysts. The results are showed in Figure 2 and Table 7.

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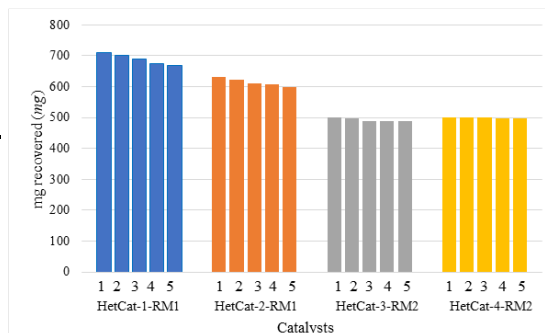
Table 7. Recycling experiments in the Michael addition of indole **1a** to **2a** with immobilized catalysts synthesized using RM1 and RM2 recovered from fluorescent lamps.

Entry	Catalyst	Y loading (mmol %)	Yield (%) 1 st	Yield (%) 2 nd	Yield (%) 3 rd	Yield (%) 4 th	Yield (%) 5 th
1	HetCat-1-RM1	0.046	43	40	33	18	6
2	HetCat-2-RM1	0.048	68	54	48	47	40
3	HetCat-3-RM2	0.046	60	57	47	37	15
4	HetCat-4-RM2	0.048	90	87	89	86	86

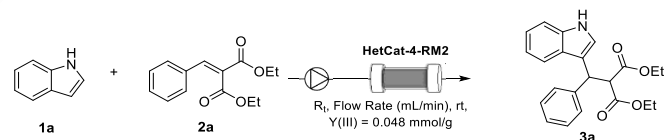
**Figure 2.** Recycling experiments in the Michael addition of indole **1a** to **2a** with immobilized catalysts

After four cycles, catalysts derived from RM1 lost completely the catalytic activity, while the catalyst prepared using the RM2 treated with 6 equiv. of trifluoromethanesulphonic acid (HetCat-3-RM2) started to lose the catalytic activity after the third recycle. The best catalyst is HetCat-4-RM2 that after four recycles maintained the same catalytic activity (Figure 3).

The best catalyst, HetCat-4-RM2 was employed for studies under flow conditions. The heterogeneous Y(III) catalyst was introduced into a tubular Omnifit EZ column 10MM/100MM 1xF 1xA reactor, provided with Teflon inlet and outlet capillary tubes.

**Figure 3.** Recycling experiments: for each catalyst, amount of catalyst recovered after each cycle is reported.

The packed bed reactor was inserted in the Asia Syrris Premium system to perform the flow experiments (Figure 4). At first the residence time was evaluated using the Pulse method,^[14] to be 18 min \pm 2 min using a flow rate of 0.05 mL/min. The Michael addition of indole and diethyl 2-benzylidenepropandionate derivatives was performed collecting the products in vials, and analysing them by benchtop ¹H-NMR, to determine the yield, using 1,3,5-trimethoxybenzene as internal standard. The yield was confirmed by the isolation of product (Scheme 5, Table 8).

**Figure 4.** Packed bed reactor in the Asia Syrris Premium system.**Scheme 5.** General Michael addition under continuous flow conditions.**Table 8.** Optimization of Michael addition under flow conditions using HetCat-4-RM2

Entry	Residence time R_t (min)	Flow rate (mL/min)	Void Volume (μ L)	Yield (%)
1	12.5	0.072	900	78 (77)
2	18	0.05	900	79 (79)
3	36	0.025	900	67 (62)

The results in the brackets represent the isolated yield.

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After every test in flow the catalyst was washed by flushing CH_3CN for 1 h at the flow rate of 0.5 mL/min. After the screening of different flow rates and consequently residence times, the Productivity (mmol/h) and Space Time Yield (mmol/mL*h) were calculated. The metrics show that in-flow reactions have Productivity values 12-30 times higher than the batch transformations, while Space Time Yields for the continuous flow process were 36-84 times higher than batch process (Table 9).

Table 9. Michael addition: Productivity (mmol/h) and Space Time Yields (STY) (mmol/mL*h) for flow process

Entry	Rt (min)	Productivity ^[a] (P)(mmol/h)	RF ^[b] P	STY ^[c] (mmol/mL*h)	RF ^[d] STY
1	12.5	$2.8 \cdot 10^{-1}$	30	$3.1 \cdot 10^{-1}$	84
2	18	$2.4 \cdot 10^{-1}$	25	$2.7 \cdot 10^{-1}$	71
3	36	$1.2 \cdot 10^{-1}$	12	$1.4 \cdot 10^{-1}$	36

^[a] Productivity: moles of product (calculated from isolated yield) divided by the collection time required to collect the product obtained by reaction of 250 μmol of 2-benzylidenepropandionate. ^[b] Relative factor of productivity in flow vs in batch ($P_{\text{flow}}/P_{\text{batch}}$). ^[c] STY: moles of product in reactor, divided by residence time and reactor volume. ^[d] Relative Factor of STY in flow vs in batch ($\text{STY}_{\text{flow}}/\text{STY}_{\text{batch}}$).

Table 10. Turn Over Number (TON) and Turn Over Frequency (TOF) for different residence times for the Michael addition.

Entry	Rt (min)	TON ^[a] (batch)	TON ^[b] (flow)	TOF batch (min ⁻¹) ^[c]	TOF flow (min ⁻¹) ^[d]
1	12.5		3		$2.6 \cdot 10^{-1}$
2	18	5	4	$3.3 \cdot 10^{-3}$	$2.2 \cdot 10^{-1}$
3	36		4		$1.1 \cdot 10^{-1}$

^[a] TON batch: mmol substrate converted for mmol of catalyst. ^[b] TON flow mmol substrate converted for mmol of catalyst ^[c] TOF batch indicates how many times the catalytic cycle occurs on a single site per reaction time. ^[d] TOF flow indicates how many times the catalytic cycle occurs on a single site per residence time.

TONs (Turn Over Numbers) and TOFs (Turn Over Frequencies) were also calculated for the batch and for the flow transformations and are reported in Table 10. The two parameters were determined based on a fixed mmol of limiting substrate, that is benzylidene diethyl malonate **2a**. In all the tests, under flow condition using different residence times, TONs are lower than batch because the mmols of substrate produced in one residence time were lower than the mmols of substrate produced in batch in 24 hours. The final TON for the in-flow process was not calculated because the catalyst is still active. On the other hand, the in-flow TOFs were increased 100 times compared to the batch process; indeed, using a residence time of 12.5 min the TOF in flow is the highest. Using the best conditions, the Michael addition was tested in flow for four days continuatively, obtaining 10.2 g of product **3a** (Figure 5)

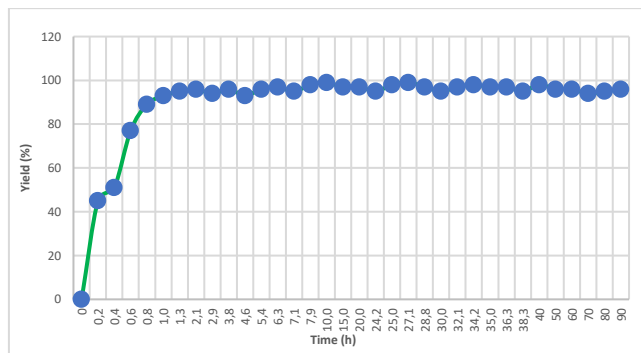
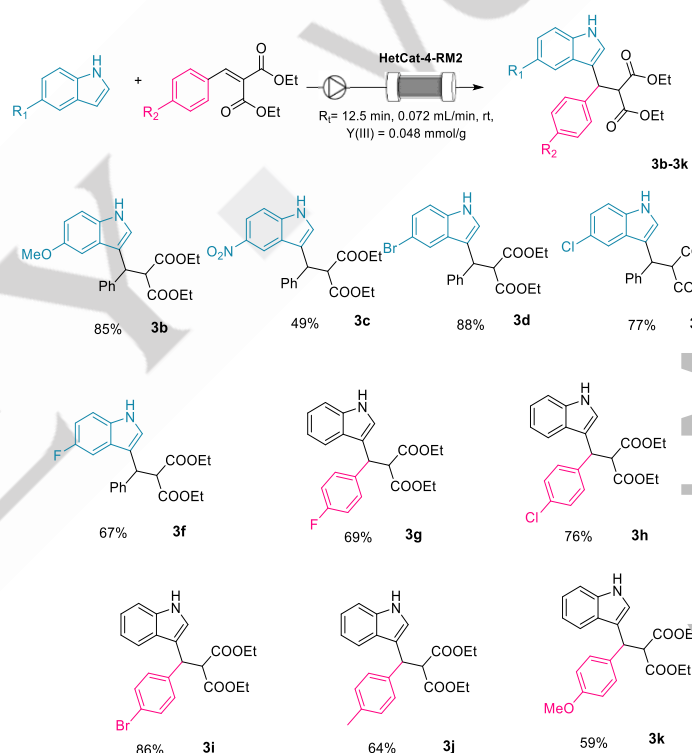


Figure 5. Model Michael reaction performed for 4 days.

In the end, using the same catalyst, a small library of derivatives was synthesised (Scheme 6).



Scheme 6. Michael addition scope under flow conditions using HetCat-4-RM2.

Also, in this case the productivity (mmol/h) and the Space Time Yield (STY) (mmol/mL*h) were calculated (Table 11). Productivity (mmol/h) of in-flow reactions was typically 38-104 times higher than in batch transformations and a good result was obtained with entry 10, in which the productivity was increased 257 times compared to batch. Space time yields (mmol/mL*h) for the continuous flow process were significantly higher (typically 106-289 times higher, in entry 10 it was improved up to 715 times).

TONs and TOFs were calculated for the reactions scope (Table 12).

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It is possible to observe that in some case the TON in flow is higher than the TON in batch because the yield in batch is low. Furthermore, the TOFs increased in flow conditions 100-1000 times compared to the batch process. Notably, the same column was used under flow condition for 109.5 hours continuously.

Table 11. Yield, Productivity and Space Time Yield in the Michael addition under flow conditions.

Entry	Product	Yield in batch (%)	Yield in flow (%)	Productivity ^[a] (P)(mmol/h)	RF ^[b] P	STY ^[c] (mmol/mL·h)	RF ^[d] STY
1	3b	78	85	3.88·10 ⁻¹	48	4.31·10 ⁻¹	133
2	3c	15	49	2.24·10 ⁻¹	144	2.49·10 ⁻¹	399
3	3d	59	88	4.00·10 ⁻¹	65	4.44·10 ⁻¹	181
4	3e	52	77	3.50·10 ⁻¹	65	3.89·10 ⁻¹	179
5	3f	76	67	3.03·10 ⁻¹	38	3.37·10 ⁻¹	106
6	3g	62	69	3.12·10 ⁻¹	48	3.47·10 ⁻¹	130
7	3h	76	76	3.47·10 ⁻¹	49	3.86·10 ⁻¹	136
8	3i	72	86	3.91·10 ⁻¹	52	4.34·10 ⁻¹	145
9	3j	27	64	2.92·10 ⁻¹	104	3.25·10 ⁻¹	289
10	3k	8	59	2.68·10 ⁻¹	257	2.98·10 ⁻¹	715

^[a] Productivity: moles of product (calculated from isolated yield) divided by the collection time required to collect the product obtained by reaction of 250 μmol of 2-benzylidenepropionone. ^[b] Relative factor of productivity in flow vs in batch (P_{flow}/P_{batch}). ^[c] STY: moles of product in reactor, divided by residence time and reactor volume. ^[d] Relative Factor of STY in flow vs in batch (STY_{flow}/STY_{batch}).

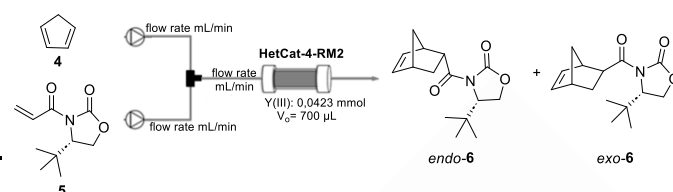
Table 12. Turn Over Number (TON) and Turn Over Frequency (TOF) Michael addition scope.

Entry	Prod.	TON ^[a] (batch)	TON ^[b] (flow)	TOF batch (min ⁻¹) ^[c]	TOF flow (min ⁻¹) ^[d]
1	3b	4	4	2.9·10 ⁻³	3.5·10 ⁻¹
2	3c	0.8	3	5.6·10 ⁻⁴	2.0·10 ⁻¹
3	3d	3	4	2.2·10 ⁻³	3.6·10 ⁻¹
4	3e	3	4	1.9·10 ⁻³	3.2·10 ⁻¹
5	3f	4	3	2.8·10 ⁻³	2.7·10 ⁻¹
6	3g	3	4	2.3·10 ⁻³	2.8·10 ⁻¹
7	3h	4	4	2.5·10 ⁻³	3.1·10 ⁻¹
8	3i	4	4	2.7·10 ⁻³	3.5·10 ⁻¹
9	3j	1	3	1.0·10 ⁻³	2.6·10 ⁻¹
10	3k	0.4	3	4.0·10 ⁻⁴	2.4·10 ⁻¹

^[a] TON batch: mmol substrate converted for mmol of catalyst. ^[b] TON flow mmol substrate converted for mmol of catalyst ^[c] TOF batch indicates how many times the catalytic cycle occurs on a single site per reaction time. ^[d] TOF flow indicates how many times the catalytic cycle occurs on a single site per residence time.

To further demonstrate the versatility and the applicability of the supported raw mixture under flow conditions, the Diels-Alder

cycloaddition between cyclopentadiene **4** and 4-(S)-3 acryloyl 4-tert-butyl 2-oxazolidinone **5** was tested, Scheme 7.



Scheme 7. Diels Alder cycloaddition under continuous flow conditions.

Table 13. Isolated yields and diastereoselectivity of the Diels Alder reaction under continuous flow conditions.

Entry	Residence time R _t (min)	Flow rate (mL/min)	d.r	Yield (%)
1	7	0.1	83:17	32
2	14	0.05	82:18	73
3	28	0.025	82:18	82

The diastereomeric ratio was evaluated by ¹H-NMR. Subsequently, the mixture of two diastereomers was purified by column chromatography. The best result was obtained using a residence time of 14 min, as confirmed by the Productivity and the Space Time Yield reported in Table 14. Productivities (mmol/h) of in-flow Diels-Alder cycloaddition were 16 to 28 times higher than in batch transformations, while space time yields (mmol/mL·h) for the continuous flow process were improved from 12 to 20 times (see Table 14). The removal of the chiral auxiliary to afford ester **7** (Scheme 5) was then performed to evaluate the enantiomeric excess of the product that was found to be 96% e.e. in all cases (Table 15).

Table 14. Productivity (mmol/h) and STY (mmol/mL·h) calculated for the Diels-Alder cycloaddition under flow conditions.

Entry	R _t (min)	Productivity (P)(mmol/h)	RF P	STY (mmol/mL·h)	RF STY
1	7	8.8·10 ⁻¹	16	1.3	12
2	14	1.5	28	2.1	20
3	28	1.2	23	1.7	16

Table 15. Diastereomeric ratio and enantiomeric excess evaluated by HPLC on chiral stationary phase on the ester **7**.

Entry	R _t (min)	d.r	e.e _{endo} (%)
1	7	83:17	96
2	14	82:18	96
3	28	84:16	96

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Conclusion

Due to the increase of technological devices and their continuous improvement, WEEE disposal has been risen in the last years. For instance, 53.6 million tons were generated worldwide in 2019 as WEEE. Furthermore, with more than 12 million tons per year, Europe ranks third only behind Asia (24.9 Mt) and Americas (13.1 Mt) in terms of E-waste, according to The Global E-waste Monitor 2020. The growing trend seems to be unchanged with a prediction of 74 Mt by 2030. Nevertheless, only < 18% of these E-waste was collected and recycled.^[15] Reducing the amount of hazardous materials in waste electrical and electronic equipment (WEEE) is crucial since improper handling of these materials can lead to serious health and environmental issues. To address these problems, the manuscript represents a proof of concept for a new approach to this WEEE management contributing to a circular economy and enhance resource efficiency. The strategy aims fit perfectly with the two pieces of legislation which have been put in place in Europe: The Directive on waste electrical and electronic equipment (WEEE Directive)^[15] and the Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment.^[16-17] It was demonstrated that is possible to use the recovered mixtures of rare earth elements, from E waste, to promote organic chemical transformations, including highly stereoselective reactions. The possibility to immobilize the material on silica and to build packed reactors were also established, leading to the preparation of a cartridge that maintained its catalytic efficiency for more than 4 days of continuous running.

Supporting Information

See the Supporting Information for: synthetic procedures of starting materials, experimental details on catalytic reactions, characterization data for products, NMR spectra for all described compounds, HPLC chromatograms. Additional references cited within the Supporting Information.^[18-22]

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Keywords: rare earth elements • recycle • stereoselective catalysis • raw mixtures • packed bed reactor

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GRAPHICAL ABSTRACT

Raw mixtures of Rare Earths Elements, REE, recovered by E-waste, were used in the synthesis of highly valuable compounds. Yttrium rich waste from fluorescent lamp catalyzed stereoselective reactions. A cartridge, prepared with raw mixtures immobilized onto silica, maintained its catalytic efficiency for more than 4 days of continuous running.

