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FIREFLY

Synthesis of catalysts using recycled metals obtained from GDEx process

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Motivation

The **chemical industry** plays a vital role in the European economy. In 2022 it **generated around 760.4 billion euros** in chemical sales [a]. 90% the conversion of materials into a wide range of products relies in the use of **heterogeneous catalysis**. They may contain precious metals such as palladium (Pd) and platinum (Pt).

For Pt and Pd extraction has been report that mining energy consumption can reach 1244 MJ/t rock and GHG emissions might surpass the 96.6 Mt CO2−e/year by 2050 [b]. Additional environmental impacts of mining noble metals are listed in Table 1

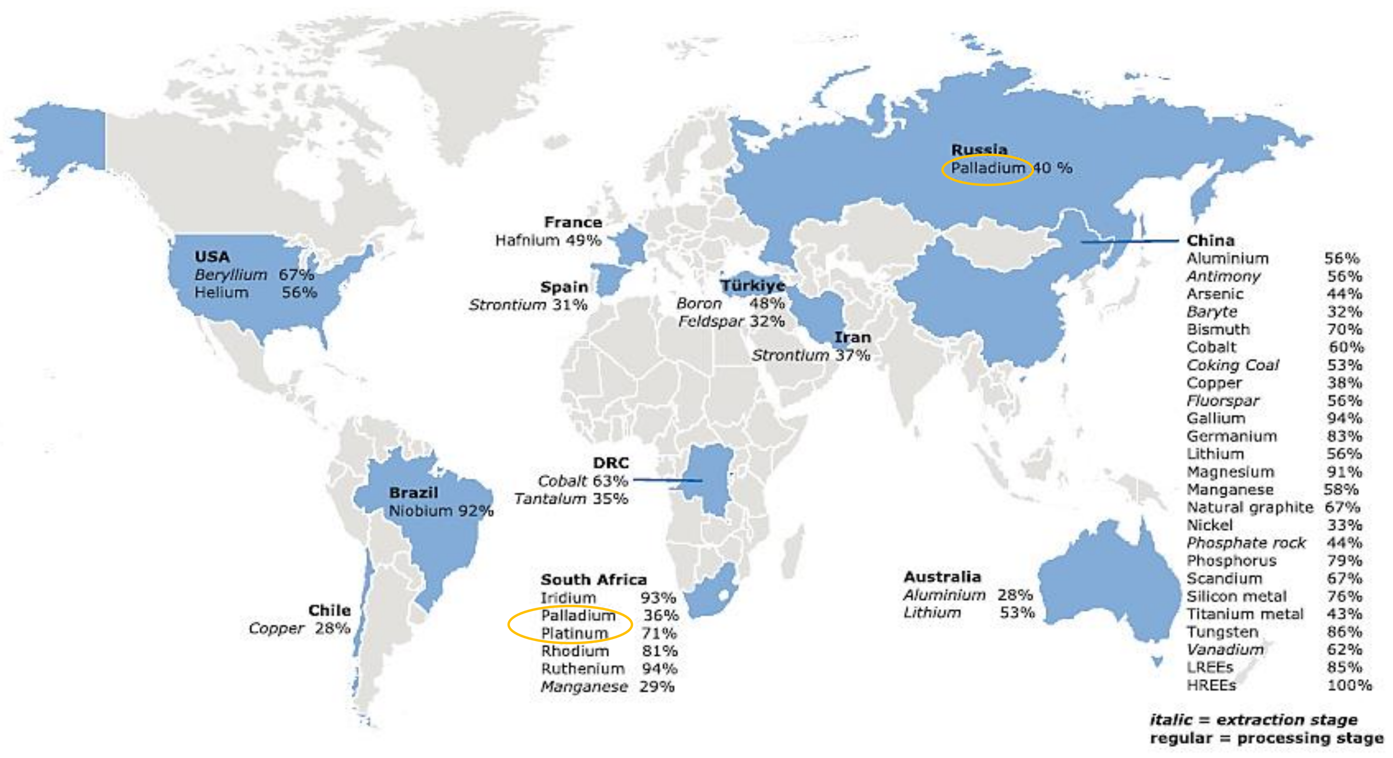


Figure 1. Critical raw materials for the EU in 2023 (European Commission, 2023)

Table 1. Impact for the primary production of 1g of metal. International Platinum Group Metals Association (IPA 2023)

Impact category	Platinum	Palladium
Global warming potential (kg CO_2 eq. /g)	31.70	22.40
Acidification potential (kg SO_2 eq. /g)	0.871	1.601
Eutrophication potential (kg PO_4 eq. /g)	0.018	0.011
Primary energy demand (MJ/g)	421.9	329.7
Photochem O3 creation potential (kg C_2H_6 eq. /g)	0.037	0.067
Blue water Consumption (kg /g)	278.9	207.2

Moreover, the European Commission in 2023 classified those noble metals as critical raw materials for the EU (see the main global producers in Figure 1). Thus, it is required that Europe is committed to achieve carbon neutrality while acquiring material sovereignty. A **decisive step** in this matter is the resource **circularity in the chemical industry.**

HOW TO RECYCLE ? By Gas-Diffusion Electrocrystallization (GDEx)

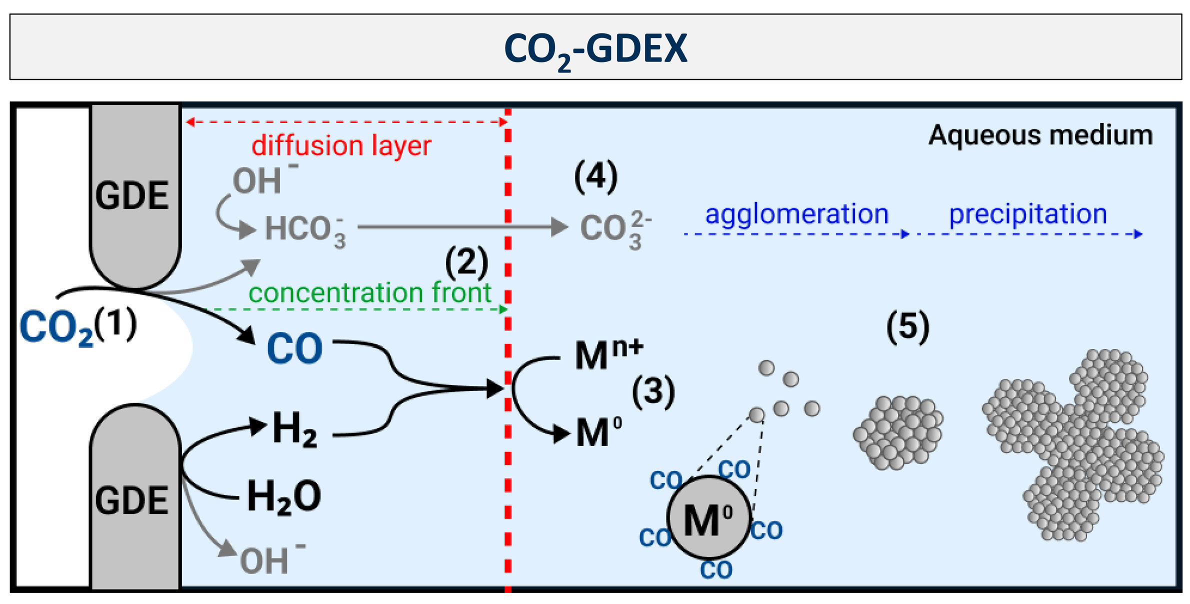
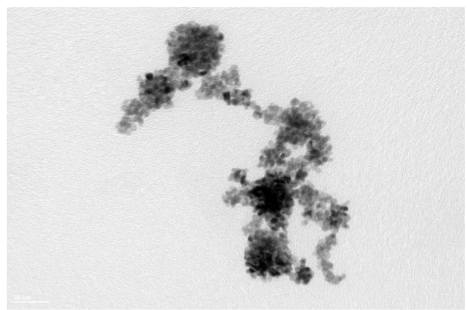
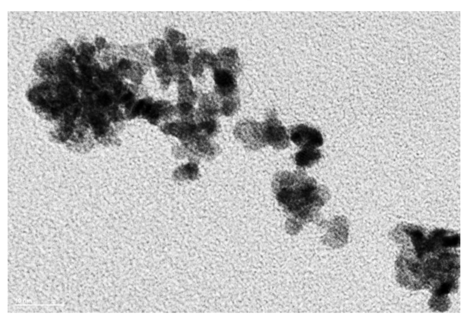


Figure 2. Representation of the key features of GDEx process[c]

GDEx is an electrochemically driven process for the reactive precipitation of metals in solution with oxidizing or reducing agents produced in-situ by the electrochemical reduction of a gas, in a gas-diffusion electrode. The nature of the product will depend on the supplied gas. When O_2 is reduced, H_2O_2 and OH– are produced, and metal (hydro)oxide nanoparticles are formed. If CO_2 is reduced, CO and H_2 are produced, and metallic nanoparticles are synthesized[c].



Pt-NPs-PVP 1g/L



PtPd-NPs-PVP 1g/L

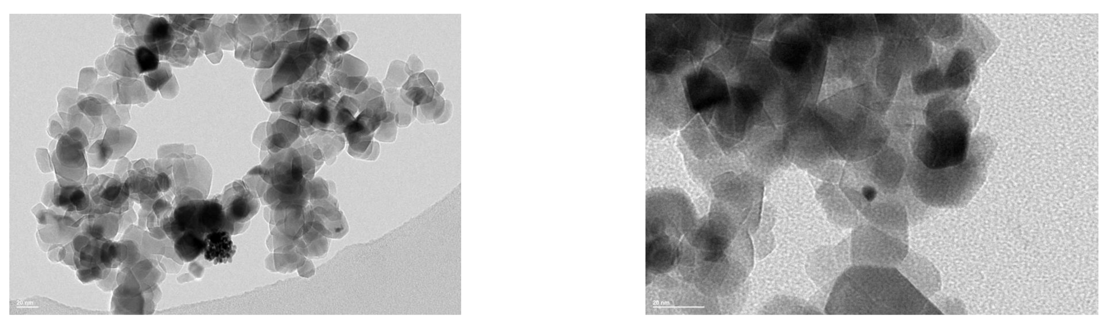
Preliminary results

Synthesis of catalysts

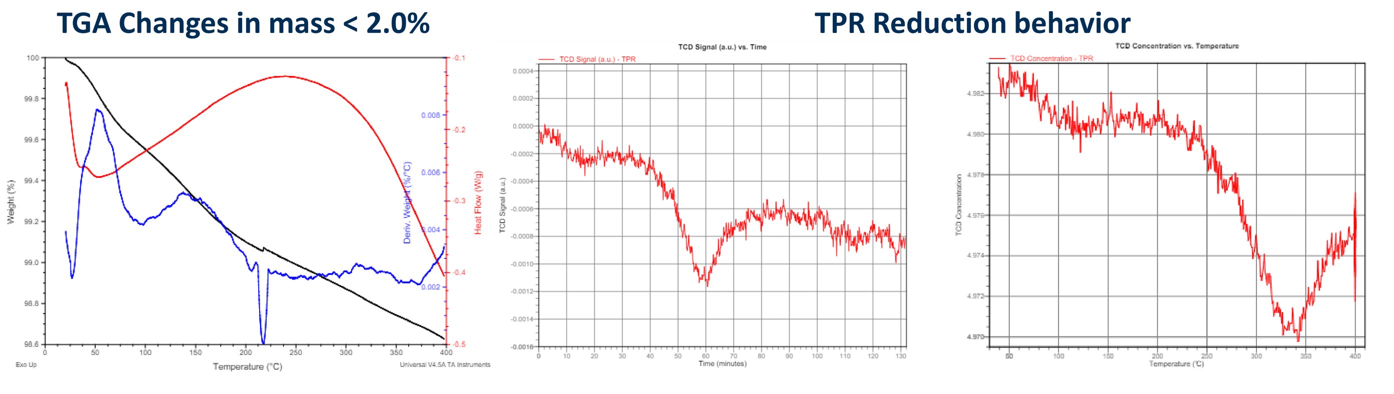
Reference catalysts were synthetized by **sol-immobilization technique** using commercial precursors. While catalysts using recovered metals were prepared by **sonication technique**[d]. TiO_2 was used as support.

Table 2. Prepared catalysts

Catalyst	Theor. load. Pd (wt.%)	Theor. load. Pt (wt.%)
SC- VITO-GDEX-002	0.0	0.5
SC- VITO-GDEX-003	0.1	0.5
SC- VITO-GDEX-004	0.2	0.5
SC- VITO-GDEX-005	0.8	0.5
Pt3Pd3 GDEX	0.2	0.5
Pt GDEX	0.0	0.5



Pt/TiO_2 agglomeration size up to 20 nm



Test of catalysts

Hydrogenation of levulinic acid (biomass derived molecule) to produce γ-valerolactone (GVL)

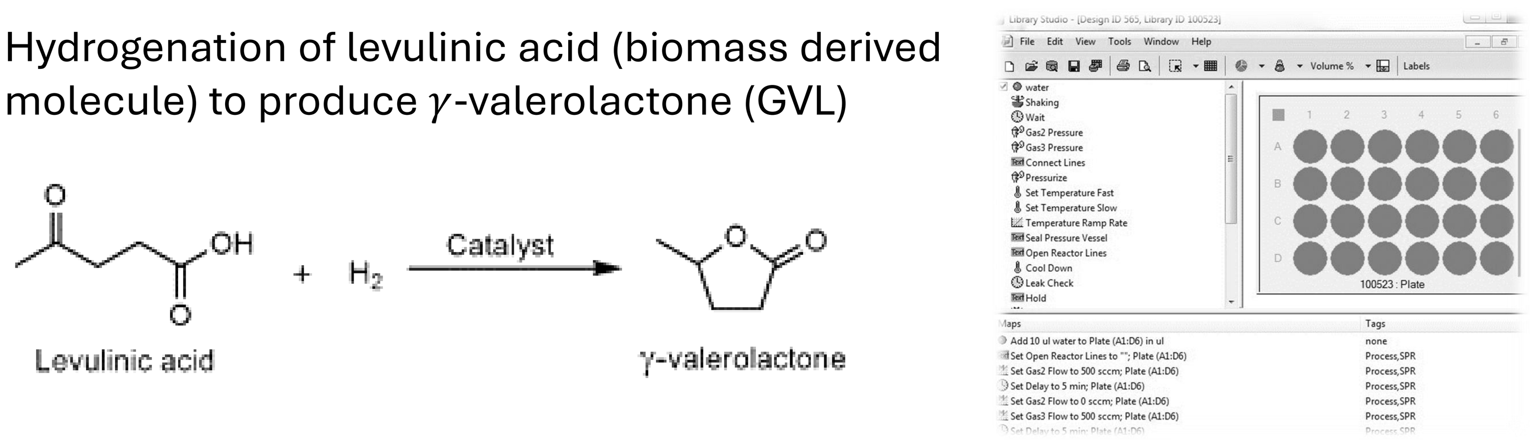


Figure 3. Reaction and interface of the Library Studio and steps for hydrogenation of levulinic acid

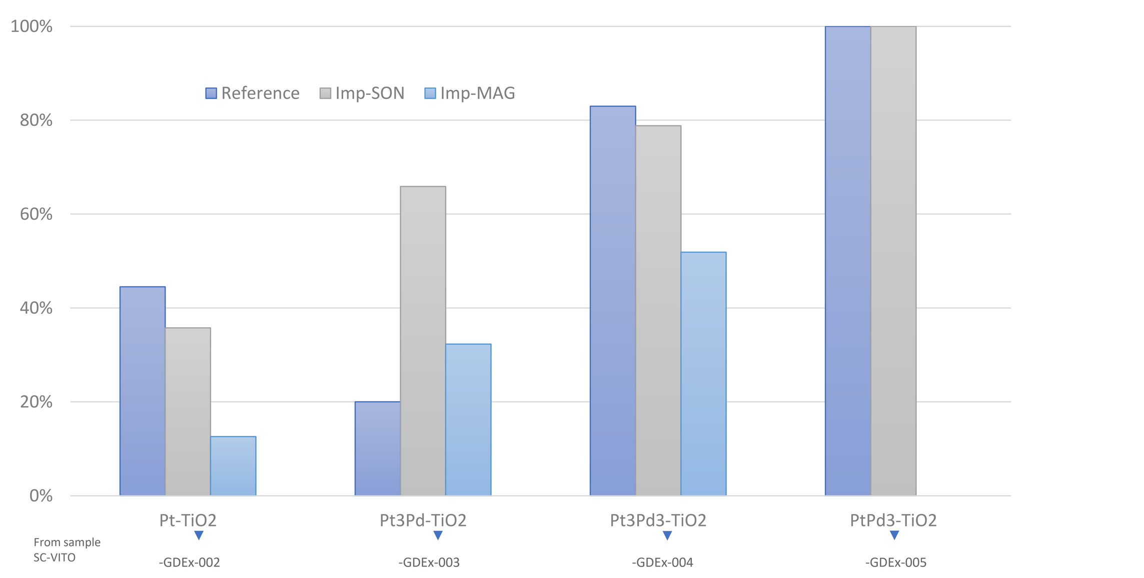


Figure 4. Comparison of the conversion between reference catalysts obtained by sol-immobilization method and the catalysts synthetized by impregnation-sonication (Imp-SON) and impregnation-magnetic stirring (Imp-MAG) using metals of GDEx process. Reaction conditions 200°C, 30 bar H2, 1ml of 10 wt.% LA in H2O, 10 mg catalyst.

Conclusion and Outlook

The deposition of PtPd3 nanoclusters on TiO_2 (0.5 wt.% Pt and 0.8 wt.% Pd) offered good performance, equally to the reference catalyst, it offered **total conversion of levulinic acid** towards GVL; the deposition of bimetallic particles seemed to enhance the catalytic activity. Monometallic catalysts (0.5 wt.%Pt/ TiO_2) reached less than 50% conversion. The support itself did not present significant catalytic activity.

Further work should be conducted to improve the anchoring of the particles to the surface of TiO_2 and other supports.

[a]Statista Research Department (2024). Chemical Industry: Chemical industry in Europe - statistics & facts https://www.statista.com/topics/9515/chemical-industry-in-europe/#topicOverview Accessed May 2024

[b]Glaister, B. J., & Mudd, G. M. (2010). The environmental costs of platinum–PGM mining and sustainability: Is the glass half-full or half-empty?. Minerals Engineering, 23(5), 438-450. https://doi.org/10.1016/j.mineng.2009.12.007

[c]Martinez-Mora, O., Pozo, G., Leon-Fernandez, L.F., Fransaer, J., Dominguez-Benetton, X.: Synthesis of platinum group metal nanoparticles assisted by CO2 reduction and H2 cogeneration at gas-diffusion electrodes. RSC Sustain. 1, 454–458 (2023) https://doi.org/10.1039/D3SU00046J

[d]Romero, D., Oropeza, F., Rigutto, M., Hensen, E.J.M. (2022). Influence of 12 polyvinylpyrrolidone as stabilizing agent on Pt nanoparticles in Pt/H-BEA catalyzed hydroconversion of n-hexadecane. Fuel 317, 123506 https://doi.org/10.1016/j.fuel.2022.123506