



SILCO Project: Waste-derived SiLiCa-based porous solids for Carbon diOxide capture, storage and re-use catalytic technology

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Significance and Relevance.

SILCO Project exhibits the potential to address both environmental and industrial challenges through innovative resource utilization. By transforming a hazardous industrial by-product hexafluorosilicic acid (FSA) into high-value silica, it advances the circular economy by converting waste into functional porous support for adsorption and heterogeneous catalysis applications. Waste-derived Silica produced as such, showing tunable porosity and surface area, are functionalized and tested as Dual-Function Materials (DFMs). DFMs integrate CO₂ adsorption and catalytic methanation functionalities, contributing to decarbonization strategies by enabling CO₂ capture and conversion into renewable methane, thus offering a sustainable and economically viable solution for CO₂ mitigation.

Preferred and 2nd choice for the topic: CO₂ Utilization and Recycling

Preferred presentation: Poster

Introduction and Motivations

Carbon dioxide remains one of the major responsible for the ongoing climate change, and the need to take urgent action to face this threat has motivated the scientific community efforts to develop efficient and cost-effective decarbonization strategies such as CO₂ Capture, Storage and Utilization (CCSU) systems. Among various technologies that have been developed to capture CO₂, adsorption and conversion by solid porous materials and catalysts is presented as a promising sustainable solution¹. On the other side, there is a growing focus on developing sustainable processes that promote resource efficiency, prevent waste generation, and encourage the re-utilization of industrial waste by-products. Indeed, a hazardous by-product of aluminum fluoride and hydrofluoric acid industrial production is hexafluorosilicic acid (FSA, H₂SiF₆). FSA, as a co-product with limited applications, could be recovered and reused as a silicon-source for the production of silica with defined morphological and structural properties for catalytic support or sorbent applications.

In this frame, SILCO Project (PRIN2022PNRR-P2022SZANL) aims to integrate a zero-waste, innovative, and sustainable technological solution to use FSA for the production of silica. The integration deals with the modification of the waste-derived silica recovering process to produce morphologically controlled SiO₂ supports, which would be functionalized for application in sorbent (CCSU) and/or catalytic (green-fuel production) routes (Fig. 1). Among the different CO₂ hydrogenation strategies, the catalytic route to renewable methane through Sabatier reaction ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$) is favorable due to its high efficiency. With all these concepts, Dual Functions Materials (DFM)² based technology, acting as both as solid adsorbents for capture CO₂ and as catalysts for fuel production upon H₂ exposure, is promising. DFMs operate in cyclic alternating conditions, schematized in Fig. 2: firstly, the material is exposed to CO₂-containing gas stream until saturation (carbon capture function due to alkaline and/or earth-alkaline catalytic material functionalization) and, secondly, a regeneration phase is carried out exposing the DFM to a H₂ stream to convert CO₂^{adsorbed} into CH₄ (hydrogenation function typically exploited by the incorporation of Ru or Ni). In literature, successful DFM consist of Ru-dispersed and Alkaline-(-earth)doped Al₂O₃-supported materials³.

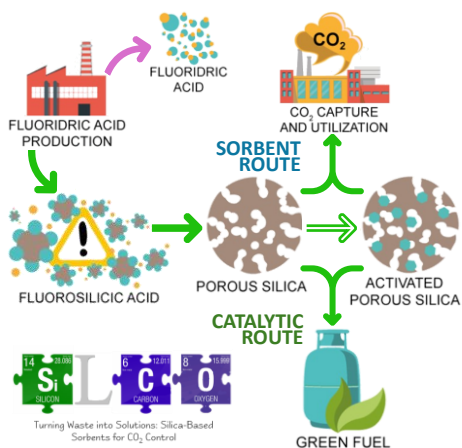


Figure 1. SILCO Project strategic development.

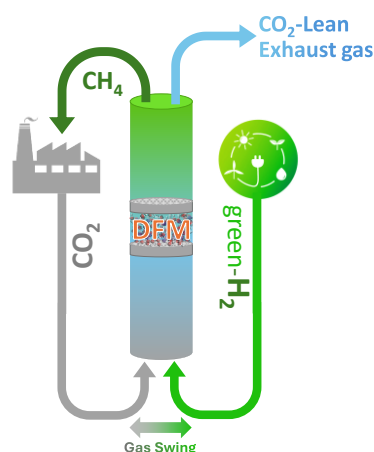


Figure 2. Schematic representation of alternating cycling condition process.

Results and discussion

Silica supports of controlled morphology, size, and porous structure, are synthesized in the presence of templates such as PEG, CTAB, and Pluronic-P123 and have been deeply characterized by FT IR spectroscopy, microscopies (SEM-EDX, HR-TEM-EDX), N₂-sorption, XRD, XPS, CO₂-TPD, inter alia. Acidity and surface properties have been also studied and compared to reference commercial materials. The supports will be then impregnated incorporating Ru (0.5% wt), and different Alkaline(-earth) oxides (i.e. Ba, Ca, K)³. The same preparation method has been used to obtain reference catalysts based on commercial SiO₂. FT-IR superficial characterization shows in case the presence of exposed silanol groups. Preliminary results obtained during the reduction of CO₂ with H₂, show that the CO₂ conversion over Ru-Ba catalysts does not depend on the support (Al₂O₃ or SiO₂); moreover, Ru-Ba/SiO₂ presents higher selectivity towards methane in respect of Ru-Ba/Al₂O₃ with the same composition (Fig. 3A,B).

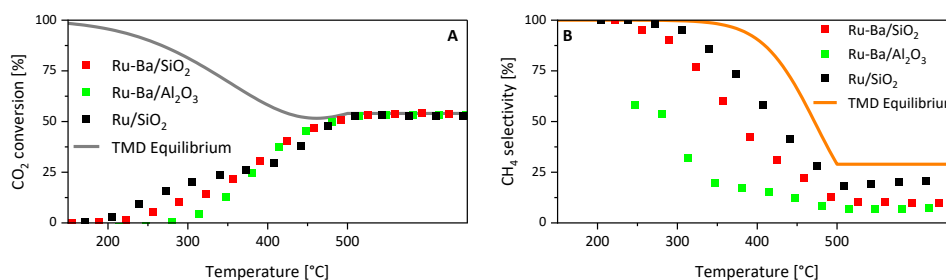


Figure 3. Results of TPR experiment: temperature ramp (from RT to 500°C @10°C/min) in CO₂ (1% v/v) + H₂ (4% v/v) balance He; A) CO₂ conversion; B) CH₄ selectivity.

Ru(0.5% wt)-Ba(16% wt)/SiO₂ has also been tested both in the adsorption of CO₂ and in its subsequent reduction. The catalyst at 150°C is able to adsorb near 230 μmol/g_{cat}, while during the reduction with H₂ only 63 μmol/g_{cat} of CH₄ are produced. This suggests that some carbonates remain on the surface that doesn't participate to the methanation reaction.

References

1. M. Sai, D. Ponnamm, K. Kumar, B. Kumar, A. Abdullah, *RSC Advances* **2021**, 11, 12658-12681.
2. M. Duyar, M. Arellano, R. Farrauto, *Applied Catalysis B: Environmental* **2015**, 168-169, 370-376.
3. A. Porta, R. Matarrese, C. Visconti, L. Lietti, *Energy&Fuels* **2023**, 37, 7280-7290.
4. www.silco.polimi.it

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