Steel slag as a highly efficient catalyst for hydrodeoxygenation of fatty acids: from a residue to a precious material for renewable fuels production

Stefano SAVINO[1,*], Giuseppe GUGLIELMO[2], Rosella ATTROTTO[2], Elena GHEDINI[3], Michele CASIELLO[1], Fiorenza FANELLI[1], Lucia D'ACCOLTI[1,3], Angelo NACCI[1,3]

[1] ICCOM-CNR, SS Bari, Via Orabona 4, 70126 Bari, Italy.

[2] Research and Development Department, Acciaierie d'Italia S.p.A., SS Appia km 648, 74123 Taranto, Italy.

[3] Chemistry Department, Università degli Studi di Bari Aldo Moro, 70125 Bari, Italy.

** stefano.savino@iccom.cnr.it*

Significance and Relevance

Steel slag, the abundant and cheap residue of steel industry, was found to be an active and highly selective catalyst in the hydrodeoxygenation (HDO) of fatty acids. This material, not always recyclable, proved to function in the pristine state (without any chemical and thermal pre-treatment), truly promoting the hydrothermal conversion of palmitic and stearic acids into the corresponding alkanes (C16 and C18) with a selectivity higher than 90%.

Preferred and 2nd choice for the topic:

- *Green chemistry and biomass transformation, renewable resources conversion.*
- *Sustainable and clean energy production and transport*

Preferred presentation: Poster

Introduction and Motivations

The global transition towards sustainable energy and the need for reducing greenhouse gas emissions (GHG) have prompted extensive research into renewable fuels[1]. Among various biomass feedstocks, fatty acids (FAs) have attracted attention due to their abundant availability and potential for conversion into high-energy hydrocarbons[2]. One of the most promising methods for upgrading FAs is hydrodeoxygenation (HDO), a catalytic process that removes oxygen from long carbon chains of carboxylic acid functionalities. The HDO reaction of fatty acids generally requires harsh conditions (200-450 °C, under P_{H_2} in the range of 4-12 MPa), and either noble or non-noble metal catalysts, preferentially anchored on supports (zeolites, alumina, silica etc.) and assembled as sulfided, bimetallic, or alloy form[3].

In this context, very intriguing appears the use of steel slag, an abundant and cheap residue of steel industry that seems to be a candidate for large-scale applications. Although the steel slags are already recycled up to 80 %, their use is for the most as inert material in the civil sector[4]. However, by virtue of their composition rich in metals, a better way to exploit this material is to transform it into an efficient and recyclable catalyst[5].

Our previous studies have already shown that steel slag displays good catalytic properties in the energy field, promoting the CO_2 photoreduction to solar fuels[6,7] and the transesterification of triglycerides[8] to give FAMEs. In this context, we predicted that this residue of industry can become a precious HDO catalyst, thus widening the range of applications of this material to a catalytic field where it has never been employed.

Materials and Methods

Steel slag was provided by "Acciaierie d'Italia," the only Italian steel producer based on integrated steel production cycle (main plant located at Taranto, Italy). Reactions were conducted in a stainless-steel reactor monitoring pressure and temperature.

Results and Discussion

Hydrodeoxygenation conditions were chosen based on the results coming from a literature[9] survey. The experimental set-up has been calibrated to handle 100 - 500 mg of fatty acid, under a hydrogen pressure of 16 bar, using the largest grain slag available. From the preliminary experiments conducted on two representative substrates, namely palmitic (PA) and stearic acid (SA), encouraging results have emerged, attested by a complete and highly selective conversion (>90%) of model fatty acids into the corresponding HDO products, hexadecane (C16) and octadecane (C18). Next, palmitic acid was selected as the substrate for carrying out further investigations, mainly aimed at studying the factors affecting the reaction course.

At first, the influence of substrate/slag amount ratio was monitored. The expected lower catalytic activity (due to the large granule sizes) was exploited to magnify the influence of such parameter as shown in Figure 1a. A very low conversion was observed with a substrate/slag ratio of 5:3, suggesting an inhibiting effect of the massive amounts of PA substrate adsorbed on the catalyst surface compared with the poor number of available active sites. By reversing the ratio in favor of the slag, conversions increased until reaching completeness with a 1:3 ratio. The blank experiment, conducted without the slag, confirmed that this material is truly a catalyst for the process.

The influence of the particle dimensions was deeply investigated using five different slag range sizes through proper grinding and sieving processes (steel slag as it is, and four fractions separated according to grain size). As expected, conversion increased with the decrease of the average granule dimensions, reaching an 80% of conversion with the smallest grains of slag (Fig. 1b). Temperature also affected HDO reaction in the predictable manner. To magnify the influence of such parameter a higher substrate/slag ratio (5:1 wt/wt) and the smallest slag sizes (210-90 µm) were used, monitoring a very large temperature range within 260 – 340 °C (Fig. 2c). Higher temperatures were avoided due to the growth of undesirable cracking side-products. Expectedly, the raise of temperature improved the slag performance in a sensible manner, allowing to reach a 60% of conversion without decreasing selectivity towards HDO product.

These investigations have preliminarily shown that steel slag, provides promising catalytic properties for the synthesis of green diesel. Steel slag was shown to be effective and especially selective in the process of deoxygenation, favoring the desired pathway of hydrodeoxygenation (HDO) and minimizing the parasitic processes of cracking, decarbonylation (DCN) and wax production.

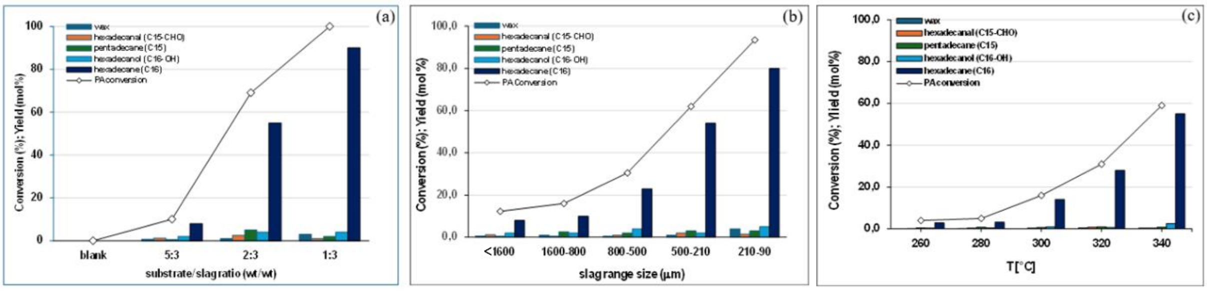

Figure 1 Studies of factors affecting HDO reaction.

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