Green syntheses of Ni-Mo-Al catalysts for deoxygenation of vegetable oil into green diesel: green metrics of syntheses and deoxygenation performances

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Significance and Relevance

To make a catalytic process sustainable in its overall life cycle, the synthesis of the needed catalyst should be as sustainable as possible too. This idea was applied to two new syntheses of Ni-Mo-Al catalysts for the deoxygenation (DO) of vegetable oils into green diesel, a process of industrial relevance in the energetic transition. Both methods aimed to fulfil some principles of Green Chemistry and Green Engineering: in one case, by avoiding the use of any solvent; in the other, by tending to implement a "one-pot" method. Sustainability performances of catalyst syntheses were evaluated by some green metrics such as: Effectiveness Ratio (R_{eff}); Reaction Mass Efficiency (RME); Mass Productivity (MP); Energy Intensity (EI). DO catalytic tests were performed too.

Preferred and 2nd choice for the topic:
Green chemistry and biomass transformation, renewable resources conversion
Sustainable and clean energy production and transport (2nd choice)

Preferred presentation: Oral preferred

Introduction and Motivations

The ACS' twelve Principles of Green Chemistry [1] and twelve Principles of Green Engineering [2], among several recommendations, suggest limiting the usage of solvents or the number of steps in chemical syntheses to improve the sustainability of related products. This approach can be applied to the synthesis of catalysts too: the improvement in the sustainability of the catalyst synthesis might be beneficial to the overall sustainability of the process in which the catalyst is involved.

The heterogeneous catalytic deoxygenation (DO) of fatty biomasses (e.g., vegetable oils) was taken as a case of study to evaluate this approach. DO converts fatty biomasses and H_2 into alkanes known as green diesel (carbon atoms in the alkane molecule from 15 to 18) [3].

A formulation of the DO catalyst in terms of ratios between NiO, MoO_3, Al_2O_3 was established, and two new synthesis methods were developed:

(i) a Solventless synthesis (OM, "Oxides Mixed") involved calcinations of Ni, Mo, and Al precursor salts and the mechanical mixing of resulting oxides. (e.g., fulfilling with principle 5 of Green Chemistry "solvents and auxiliaries"); it is under patenting procedure [4];

(ii) a One-pot synthesis (OMA = "Oxides Mixed in Aqueous medium") involved the wet-mixing of Ni, Mo, and Al precursor salts in an aqueous medium, and one overall calcination. (e.g., fulfilling with principle 4 of Green Engineering "maximize efficiency").

The sustainability performances of these two synthesis methods were compared by estimating green metrics. The solid catalysts were characterized. The DO catalytic performances were evaluated for the two OM and OMA catalysts.

Results and Discussion

The XRD (X-Ray Diffraction) characterization of the two catalysts OM and OMA (not shown) evidenced the formation of different crystalline phases: OM contained Ni, Mo and Al not combined one to the other; OMA contained some crystalline phases combining Ni-Mo and Al-Mo.

The sustainability of the two syntheses of OM and OMA was evaluated by four green metrics:

(i) Effectiveness Ratio: $R_{eff} = \frac{obtained\ mass\ of\ catalyst}{expcted\ mass\ of\ catalyst}$

(ii) Reaction Mass Efficiency: $RME = \frac{obtained\ mass\ of\ catalyst}{mass\ of\ precursor\ salts}$

(iii) Mass Productivity: $MP = \frac{obtained\ mass\ of\ catalyst}{mass\ of\ precursor\ salts + mass\ of\ solvents, reactives}$

(iv) Energy Intensity: $EI = \frac{energy\ consumed\ in\ the\ synthesis}{obtained\ mass\ of\ catalyst}$

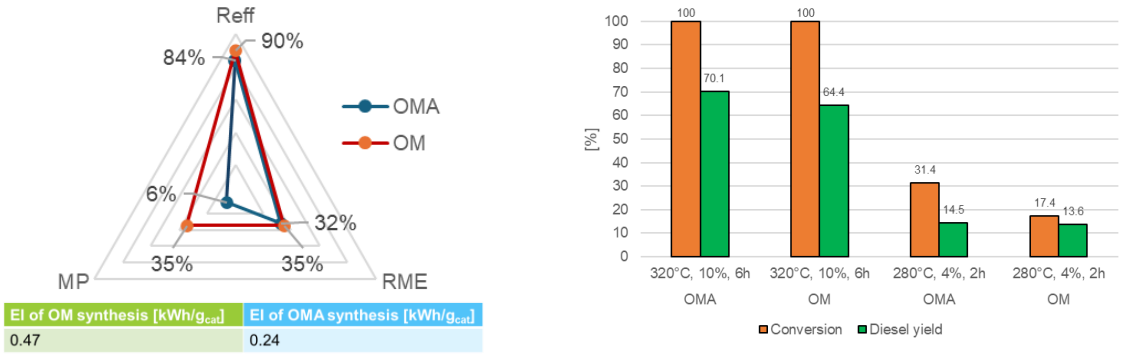
Figure 1(a) shows the comparison of the green metrics: as to "mass" green metrics (R_{eff}, RME, MP), only MP was significantly different, i.e., lower in the case of OMA synthesis because of the use of a solvent; on the other hand, OMA synthesis appeared more energetically advantageous, because of the use of only one calcination in the place of the three calcinations of OM.

The DO performances of OM and OMA were evaluated by catalytic tests on commercial rapeseed oil (2 g) in a batch laboratory-scale reactor, at two sets of conditions: {320°C-10% (catalyst/oil mass ratio)-6 h of reaction} or {280°C-4% (catalyst/oil mass ratio)-2 h of reaction}. The DO liquid product was characterized by gas-chromatographic techniques [5], to estimate:

(i) DO conversion: $\chi = \left(1 - \frac{mass\ of\ unconverted\ oil}{initial\ mass\ of\ oil}\right)$

(ii) DO diesel yield: $Y_{diesel} = \frac{mass\ of\ alkanes\ with\ 15,16,17,18\ C\ atoms}{initial\ mass\ of\ oil}$

Figure 1(b) compares catalytic performances of OM and OMA: both catalysts carried out DO satisfyingly at {320°C-10% (catalyst/oil mass ratio)-6 h of reaction}, according to χ and Y_{diesel} in the literature [3]; at the other set of conditions {280°C-4% (catalyst/oil mass ratio)-2 h of reaction}, the OMA catalyst showed a higher catalytic activity (higher χ) and a lower selectivity towards alkanes (similar Y_{diesel}) than those expressed by OM.



(a) (b)

Figure 1 Comparison between OM and OMA catalysts: (a) Radar Plot to compare mass Green Metrics and values of EI; (b) DO performances

Overall, two new green-syntheses were proposed to produce Ni-Mo-Al catalysts that worked for the DO of rapeseed oil into green diesel. Some sustainability aspects of these syntheses were evaluated: the mass green metrics favour OM, whereas energy intensity favour OMA; on the other hand, the additional mass involved in OM synthesis is water (the best choice among solvents in terms of sustainability).

References

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