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Bimetallic catalysts for the conversion of sorbitol into hydrocarbons by aqueous phase hydrodeoxygenation

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PURPOSE OF THE ABSTRACT

Depleting oils resources and environmental concerns urge us to rethink our transportation politics and to develop new efficient processes for biobased liquid fuels. Drop-in fuels like ethanol are a good temporary replacement, but face many problems when used in too high concentrations [1]. A solution to this problem would be to produce bio-based and oxygen-free alkanes which can be used as is, without engine compatibility issues.

For this purpose, hydrodeoxygenation (HDO) is a promising process. Already available at a commercial scale for the hydrotreatment of vegetal oils (C16-C22), it consists of a catalytic removing of oxygen while carrying hydrogenation of potential double bonds, producing clean, long chain alkanes.
The next challenge is now to apply HDO to lignocellulosic biomass in order to get alkanes that can be used to replace gasoline (C5-C12).

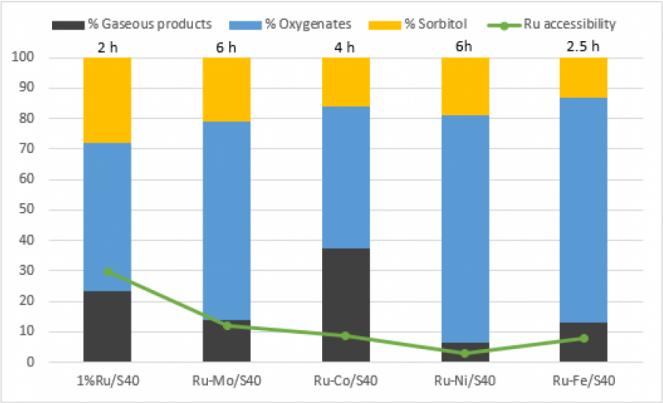
Efforts to achieve HDO of cellulose-derived sorbitol towards C5-C6 hydrocarbons have led our team to develop bimetallic catalysts that possess both acidic and reductive functionalities while being stable under hydrothermal conditions. In a previous study, formulations combining Re, Rh, Ru or Ir to a Pt/SiO2-Al2O3 (Siral 40) parent catalyst have been tested [2]. The transformation of sorbitol in aqueous phase was carried out in autoclave at 240 °C and 60 bar of H2 to discriminate the best bimetallic formulations. The addition of Ru to Pt/SiO2-Al2O3 catalyst by successive impregnation allowed to improve significantly the yield and the selectivity towards hexane, indicating a noticeable synergistic effect explained by a strong Pt-Ru interaction within the bimetallic system consisting only of small size bimetallic particles.

While platinum based catalysts have shown great overall activity, efforts are made to reduce the use of rare and expensive noble metals. In our current work, the use of non-noble metals (Mo, Co, Ni, Fe) combined with ruthenium catalysts supported on amorphous silica-alumina (Siral 40) is being investigated for the sorbitol HDO. The as-prepared bimetallic systems are characterized notably by O2 chemisorption, temperature programmed reduction, and model reactions to evaluate their acid and metal functions.

Large dispersion of Ru particles on Siral 40 is achieved via ionic exchange in basic medium between a Ru(NH3)6Cl3 precursor and the polarized SiO2-Al2O3 surface of the support. Additions of Ni and Fe to the as-prepared 1wt%Ru/SiO2-Al2O3 catalyst (molar ratio Additive/Ru = 1) are not favorable on the production of hydrocarbons and the Co-Ru formulation leads to an increase of hydrocarbons production but mainly towards methane (Figure 1). On the other hand, addition of Mo shifts the selectivity toward C5 and C6 products (Figure 2), namely pentane, hexane and hexane isomers in the gas phase, and isosorbide and 1,4-sorbitan in the aqueous phase. The synthesis process of these bimetallic catalysts also seems to have an influence on the performances in transformation of sorbitol. Further characterizations and investigations on synthesis of Ru-based catalysts modified by Mo and Co will be performed to determine the key parameters behind the observed selectivity and

enhance the performance of these catalysts.

FIGURES



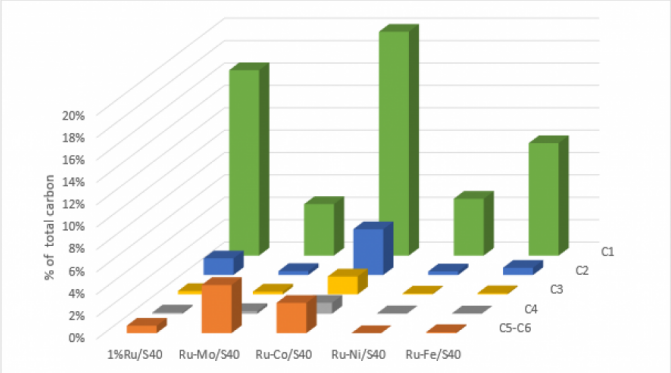


FIGURE 1

Carbon global distribution obtained at the given reaction time (corresponding to 76-89 % conversion)

Figure 1

FIGURE 2

Carbon distribution in the gas phase at 76-89 % conversion

Figure 2

KEYWORDS

bimetallic catalysts | sorbitol | aqueous phase hydrodeoxygenation | biofuels

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