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Heterogeneous catalytic hydrodeoxygenation of mucic acid in aqueous conditions

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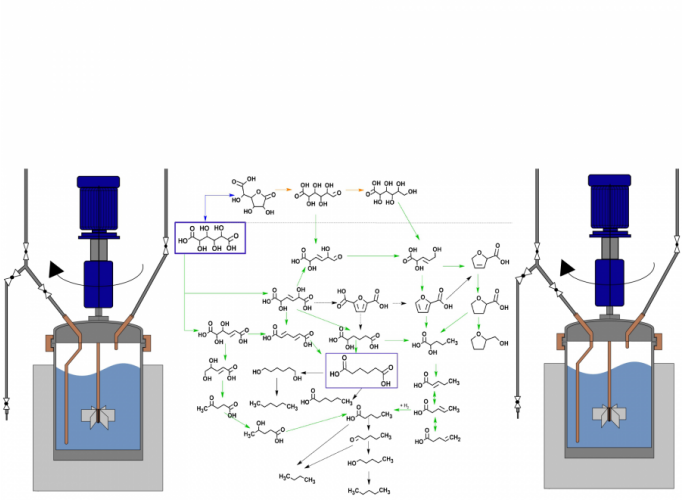
PURPOSE OF THE ABSTRACT

Recently many studies are devoted to the development of the new processes for the production of industrially important chemicals, still produced from oil. Technologically are these processes matured, but they are not environmentally friendly due to high greenhouse gas emissions. The development of new processes and new feedstocks are indispensable. One of the most important chemical is adipic acid, currently only produced from the petrobased sources. Only a few scientific researches and two patents are published on chemocatalytic conversion of aldaric acids towards adipic acid [1?3].

Hydrodeoxygenation of mucic acid (which is aldaric acid) over different heterogeneous metal catalysts (Ru, Pt, Rh, Ni, NiMo) on neutral or acidic supports (C, SiO2, Al2O3) was performed in our study in order to consider the most active catalyst for selective HDO of aldaric acid. Catalytic hydrotreatment experiments were performed in a six parallel batch high-pressure autoclave system in a three-phase regime. Mucic acid was dissolved in distilled water; additionally, solid catalyst was added in the liquid phase. In a gaseous phase, H2 was present at high pressure (5.0 MPa). Liquid samples were collected during the reaction time and analyzed by HPLC and/or LC-MS. Reactant, intermediates, and products were detected by UV detector in the range from 200 to 400 nm. The final product from reactor vessel was furthermore treated by two different protocols for GC?MS analysis in order to remove water and convert the components into more volatile derivatives.

Reaction pathway network was developed and it was subdivided into a non-catalytic and heterogeneously catalyzed part. In the absence of a catalyst, mucic acid forms an equilibrium with mucic acid-1,4-lactone, which is common in aqueous media. Lactone was detected already at room temperature. Under inert atmosphere, the only lactone was formed from mucic acid, while under high H2 pressure formation of galactonic acid and minor concentration of galacturonic acid was promoted in the absence of a catalyst. In the presence of a catalyst partially or completely deoxygenated products were formed. In the first step, H2O molecule was eliminated from mucic, galacturonic or galactonic acid (from C2-C3 or C3-C4 position) resulting in C6 diols with one or two terminal carboxylic groups. The most important detected chemicals are adipic acid and furan-based products. However, numerous molecules were detected, such as tetrahydro-2-furfuryl alcohol, 2-hydroxy hexanoic acid, 2-hydroxy pentanoic acid, levulinic acid, 2-furoic acid, 2-pentenoic acid, hexanoic acid, propanoic acid, 3-methyl-2-hydroxypentanoic acid, etc. Using cheaper NiMo catalyst at slightly higher temperatures delivered better results compared to the more active noble metal catalysts at the lower temperature. Even though NiMo/?-Al2O3 catalyst is a well-known industrial catalyst for HDO reactions, many authors pointed out that its support (alumina) is not stable in the water environment. For short time (total=3.5 h) experiments it worked very well, without any deactivation. The main issue using oxidized cellulose-based feedstock, such as mucic and glucaric acid is the solubility, which is very low (or negligible) in water, alcohols and organic solvents. The aqueous environment is eco-friendly, but on the other hand, could degrade Al2O3 structure of the catalyst support resulting in lower overall activity.

FIGURES



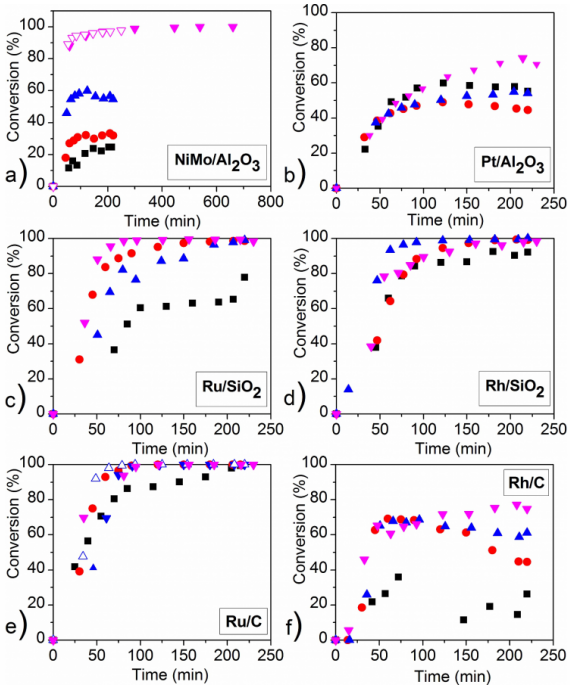


FIGURE 1

Figure 1

Parallel batch high-pressure autoclave system and proposed reaction pathway.

FIGURE 2

Figure 2

Conversion of mucic acid over transition and noble metals on neutral or acidic suports

KEYWORDS

bio-based chemicals | hydrodeoxygenation | aldaric acid | adipic acid

BIBLIOGRAPHY