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BUTANEDIOLS PRODUCTION FROM C4 POLIOLS USING HETEROGENEOUS CATALYSIS

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PURPOSE OF THE ABSTRACT

Introduction

Erythritol (ERY) is a poliols that can be easily produced by fermentation of sugars and is considered as a promising C4 intermediate obtained from biomass [1]. The most valuable products obtained from ERY hydrogenolysis are butanediols (BDOLs). 1,3-BDOL is used in food flavorings and for polyurethane and polyester resins, 1,4-BDOL as raw material for polyurethanes and polybutylene terephthalate, 1,2-BDOL is used for the production of low viscous polyester and plasticizers and the main products from 2,3-BDOL includes inks, perfumes, fumigants, etc [2,3].

The main reactions pathways of erythritol on metal catalysts involve the following reactions: C-O hydrogenolysis, C-C hydrogenolysis (to produce C2 and C3 products), dehydration (to render 1,4 anhydroerythritol) and isomerization (to form threitol). BDOLs are produced by C-O hydrogenolysis reactions via 1,2,4 and 1,2,3-butanetriol (BTOs), the consecutive hydrogenolysis of butanediols produces butanols and butane, which are less valuable products and therefore should be avoided.

The direct hydrogenolysis of ERY to produce butanediols was previously reported by Amada et al [4] using 4 wt.% Ir/ReOx/SiO₂ catalyst (Ir/Re=1); the selectivity to butanediols reached was 48% at 74.2% conversion at 100°C and PH₂=80 bar after 24 h of reaction. Some recent research [5] was reported about BDOL production from ERY on bimetallic Rh-Re catalyst supported on ZrO₂ and TiO₂ and the highest selectivity to BTOL+BDOL reached was 37% at 80% conversion in the presence of 3.7wt%Rh/3.5wt%ReOx/ZrO₂ catalyst at 200°C and 120 bar. To our best knowledge the role of support on Ir and Re catalytic properties related to erythritol hydrogenolysis to produce butanediols are lacking. Therefore, the aim of this work is to study the effect of the properties of the support on the Ir and Re species in order to get high yields to butanediols from erythritol.

Experimental

Bimetallic Ir/ReOx (Re/Ir =1) catalysts supported on SiO₂, Carbon, Al₂O₃, CeO₂, ZrO₂ and TiO₂ were prepared by successive incipient wetness impregnation. Catalysts were characterized by N₂ physisorption, CO chemisorption, TEM, XPS and FTIR of pyridine. These catalysts were tested using a Parr reactor in the hydrogenolysis of an aqueous solution of erythritol to butanediols (BDO) at 150-250°C and 25 bar H₂. Reactants and products were analyzed using HPLC (RI detector) whereas gaseous products were analyzed using a GC-MS.

Results and Discussion

The physicochemical characterization of the catalysts suggest a different distribution and oxidation state of Re and Ir species depending on the support; also the acid properties evaluated by FTIR of pyridine were different.

Preliminary results at different reaction temperature (150 to 225°C) showed that the best activity and selectivity towards BDOL were achieved when using 200°C. We compared in Figure 1 the ERY conversion vs time for the

catalysts used in this work. The catalyst activity and products selectivities were dependent on the nature of the support. Ir/ReOx/TiO₂ was the most active catalysts and reached a total erythritol conversion at about 16 h followed by the Ir/ReOx/ZrO₂; catalysts supported on SiO₂, Al₂O₃ and CeO₂ were less active at similar conditions. The products distribution is presented in Figure 2 at identical conversion (X_{ERY}=90%). Ir/ReOx/TiO₂ selectively formed butanediols with a maximum yield of 50% which is an important result comparing to those reported in literature. On the contrary, Ir/ReOx/Al₂O₃ and Ir/ReOx/ZrO₂ favored the dehydration route conducting to cyclic products due to the acidity of the support. The superior activity of Ir/ReOx/TiO₂ can be explained taking into account the species of Ir and ReOx detected by XPS and the presence of small amounts of weak acid sites that promotes undesirable reactions.

FIGURES

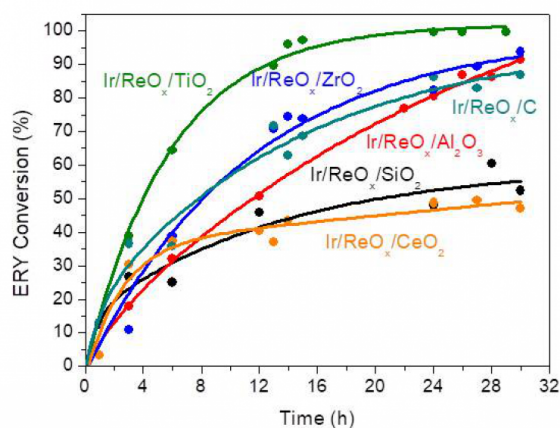


FIGURE 1

Erythritol conversion versus time

[200°C, ERY 0.4 M, PH₂= 25 bar, 600 rpm, 0.5 g of catalyst]

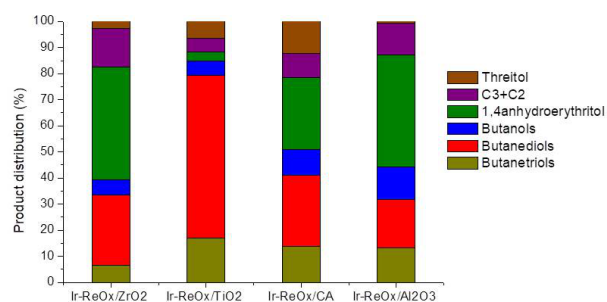


FIGURE 2

Products distribution for Erythritol conversion of 90%

[200°C, Erythritol 0.4 M, PH₂ = 25 bar, 600 rpm, 0.5 g catalyst]

KEYWORDS

BUTANEDIOLS | ERYTHRITOL | HYDROGENOLYSIS | BIOMASS

BIBLIOGRAPHY

- [1] K. Tomishige, M. Tamura, Y. Nakagawa Chem. Rec. 2014, 14, 1041–1054
- [2] X.-J. Ji, H. Huang, P.-K. Ouyang, Biotechnol. Adv. 2011, 29, 351–364.
- [3] R. Hasegawa, K. Hayashi, US 4596886, 1986
- [4] Y. Amada, H. Watanabe, Y. Hirai, Y. Kajikawa, Y. Nakagawa, K. Tomishige ChemSusChem (2012) <https://doi.org/10.1002/cssc.201200121>
- [5] A. Said, D. Da Silva Perez, N. Perret, C. Pinel, M. Besson, ChemCatChem 2017, 9, 2768–2783