Hydrodeoxygenation of biomass-derived polyols to green butadiene over Rhenium modified supported catalysts

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ABSTRACT

The present work refers to one step catalytic process of erythritol hydrodeoxygenation (HDO) to 1,3-butadiene over supported metal and mixed metal catalysts on carbon black. Catalyst screening was performed under specified reaction conditions in batch reactor. A mixed Mo-Re catalyst was the most promising one as it favored oxygen removal from the polyol to form the desired alkene. The effect of reaction parameters (reaction time, temperature, H_2 pressure, catalyst/substrate ratio) was explored over 5Mo-10Re/BC. Increased temperature and H_2 pressure promoted erythritol conversion towards 1,3-butadiene eliminating the formation of 3-butene-1,2-diol, the main intermediate. 1,3-butadiene selectivity of 93% was achieved for 41% conversion at 140 ºC, 60 bar initial H_2 pressure and 5 h reaction time. XPS measurements indicated that the super surface layer of the catalyst consists of Mo^{6+}, Re^{7+}, Re^{6+} and Re^{4+} species which are the active sites. The effect of calcination conditions was also explored indicating that the calcination atmosphere modifies catalyst structure highly affecting product distribution.

KEY WORDS: Hydrodeoxygenation, erythritol, butadiene, heterogeneous catalyst, rhenium, molybdenum

INTRODUCTION

Light olefins C_2-C_4 are considered the most important monomers in petrochemical industry, due to their numerous applications achieving the highest production volumes worldwide. Their current existing production technologies(fluid catalytic cracking, naphtha steam cracking) are highly depended on fossil-based resources releasing approximately 400 million metric tons of CO_2 pes year [1]. Propylene and ethylene are the most important olefins followed by the C_4 olefins, such as 1,3-butadiene (BD) and butenes. Among them, 1,3-butadiene is considered a crucial chemical intermediate, the production of which is mostly driven by the demand of rubbers, important raw material for automotive industry. Triggered by its increased demand along with the economic and environmental concerns related to the use of fossil-resources the development of new sustainable processes for their production has become imperative. Biomass and its derivates are environmentally friendly feedstocks and appear as interesting substitutes to fossil-based ones due to their neutral carbon footprint. Among them, sugar alcohols such as glycerol, erythritol, sorbitol etc. are considered important feedstocks in biorefineries, the valorization of which has attracted scientific interest during the last years[2].

Erythritol, an industrially fermentation product can be converted to a wide variety of products, such as 1,4-anhydroerythrtiol, butanediols and others via various catalytic processes[3]. Catalytic hydrodeoxygenation of erythritol (HDO) to produce 1,3-butadiene is an alternative albeit challenging path that has not been widely studied in the open literature. The selection of the catalytic material is of outmost importance as according to scheme 1 a notable number of products could be achieved. Targeting 1,3-butadiene, the catalyst should be active in C-O bond scission of erythritol preserving the C-C and the formed C=C bonds. In most of the cases the selection of the material can be made based on the ones applies in similar reactions of other polyols, such as

glycerol. In a previous study of our group, it was proven that molybdenum-based catalysts are ideal materials for converting glycerol to propylene at high yields highlighting the potential use of molybdenum-based catalyst in erythritol HDO [4,5]. To the best of our knowledge, the available reports in the open literature regarding 1,3-butadiene production via erythritol HDO are rare and in most of the cases rhenium-based catalysts were used as catalytic materials [6]. Therefore, a series of rhenium and mixed molybdenum-rhenium catalysts were synthesized and evaluated in a batch reactor under specified reaction conditions to favor oxygen removal. The most promising catalyst was further explored in a wide range of operating conditions to optimize the yield of the desire olefin.

Scheme 1. *Potential reaction network of erythritol conversion under hydrogen atmosphere*
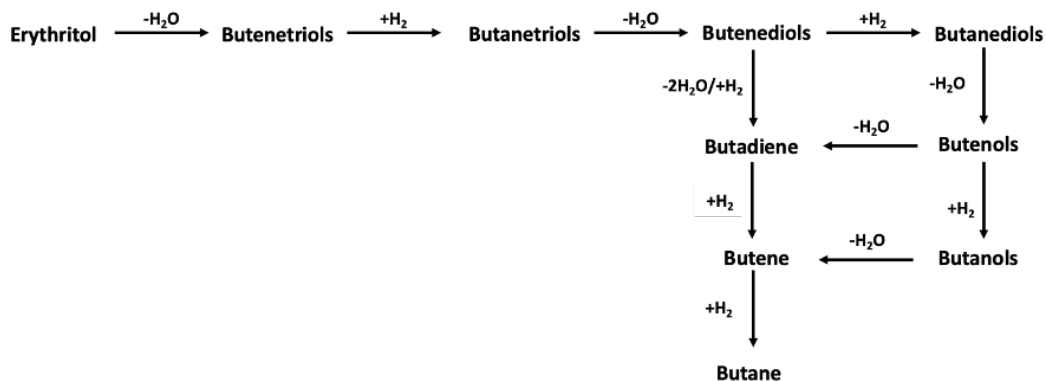
METHODOLOGY
Catalyst synthesis

Rhenium based catalysts with different Re loadings (2-5-20%, named as 2Re/BC, 5Re/BC, 20Re/BC) supported on a commercially available black carbon (BC) Vulcan XC72 were prepared by wet impregnation method as previously described [4] using ammonium perrhenate (NH_4ReO_4) as precursor. The obtained catalyst was calcined at 500 °C for 3h under N_2 flow instead of air to avoid carbon burn-off. In the case of mixed Mo-Re/BC catalysts, first the Mo/BC was impregnated following the same procedure previously described using ammonium molybdate ((NH_4)$_6Mo_7O_{24}$.$4H_2O$) as precursor followed by impregnation of Re precursor. Two mixed Mo-Re/BC catalysts were synthesized, one with 5wt% Mo and 10%wt% Re loading (named as 5Mo-10Re/BC) and another one with 10wt%Mo and 5wt% Re loadings (named as 10Mo-5Re/BC). In an effort to determine the effect of calcination atmosphere, calcination was also conducted under air flow and at lower temperature (300°C). For the catalyst calcined under oxidizing atmosphere an OXID subscript signifies the different calcination atmosphere.

Catalyst characterization

The Brunauer-Emmet-Tellet (BET) surface area and porosity of all fresh catalytic materials, as well as that of the support were determined by N_2 physisorption at 77.35K using a Quantachrome Nova 2000e analyzer.

The X-ray diffractometry (XRD) technique was employed in order to verify the crystallographic phases of both fresh and used catalysts. The X-ray diffraction patterns of the samples were obtained by using a Bruker D8 Advance diffractometers, with CuKa radiation (λ=0.15406 nm) over 2θ=10° to 90°, at a scan rate of 0.5 s/point and step 0.02°.

XPS measurements were performed on a Kratos Analytical AXIS ultra DLD spectrometer equipped with and aluminum monochromatic X-ray source (λKα=1486.6 eV). The wide scan spectra were recorded by applying 7 mA/10 kV on X-ray source with pass energy of 160 eV. High resolution (HR) regions were recorded with pass energy of 20 eV on the analyzer during a three-sweep scan applying 10 mA/15 kV on X-ray gun. Binding energy referencing was employed based on C 1 s peak at

284.6$\pm$0.1 eV for the C-C bonds. Before XPS measurements the samples were stored under vacuum and the analysis was conducted on the same day.

Catalytic experiments

Erythritol HDO activity tests were performed in liquid phase in batch reactor (80 ml) installed at Institute of Catalysis (IKFT) at Karlsruhe Institute of Technology (KIT). A PTFE (polytetrafluoroethylene, teflon) was added in the reactor to reduce the volume at half. Typically, 0.5 gr erythritol in 4.5 ml solvent (1,4 dioxane), along with 0.3 gr (unless otherwise stated) catalyst were added in the reactor with a magnetic spinner. At the end of the reaction, the gas phase was collected in a gas bag, while the liquid phase along with the catalyst was diluted with distilled water (1:10) and remained under stirring for 2 minutes to completely dissolved the remaining feed. Then, the catalyst was separated from the liquid phase through vacuum filtration. The liquid products were quantified based on the analysis by gas chromatography (Agilent 7890B) equipped with a flame ionization detector and a capillary column (Stabilwax q/integra quard 30m, 0.25 mm ID, 0.25μm). Before analysis, liquid samples were diluted 10 times with tetrahydroxyfuran (THF). Gas products were analyzed in a GC (6890) equipped with both TCD and FID detector and two columns in series/bypass configuration (Hayesep Q 2m, 2mm i.d and Molsieve 5A 80/100 2m, 2mm i.d).

RESULTS AND DISCUSSION
Catalyst characterization

The BET surface area 20Re/BC (150 m^2/g) is considerably lower than that of the support (250 m^2/g) most likely due to pore blocking of the catalyst by the metal. However, over 2Re/BC and 5Re/BC the BET is close to that of the support (274 and 219, respectively) owing to relatively low Re loading. In the case of both mixed Mo-Re/BC catalysts their similar surface area (187 m^2/g for 5Mo-10Re/BC and 182 m^2/g for 10Mo-5Re/BC).

XRD analysis was performed to examine the structure of each material. The XRD results of all Re/BC catalysts indicated that Re crystallizes mostly as Re_3O_{10}. Over 2Re/BC and 5Re/BC, it appears as broad peaks, whereas over 20Re/BC is fully crystallized indicating the catalyst structure is affected by impregnating different Re loadings. However, in every case one and extremely low intensity peak of ReO_2 is observed indicating the existence of both reduced and oxidized species. This can be attributed to the applied calcination conditions, as the presence of black carbon in combination of N_2 atmosphere at high temperatures promotes the reducibility of the oxides. On the other hand, the XRD spectra of both Mo-Re/BC catalysts resemble that of 20Re/BC and show mostly diffraction peaks that are characteristic to Re_3O_{10}, while low intensity peaks of ReO_2 and MoO_2 are also observed. However, the intensity of the peaks becomes less intense over both Mo-Re/BC compared to 20Re/BC probably due to the decrease in the crystallite size (20Re/BC: 17nm, 5Mo-10Re/BC: 14.10 nm, 10Mo-5Re/BC: 14nm) implying a better dispersion of the metals on the surface.

Catalytic experiments

The catalytic performance of all the materials in erythritol HDO was evaluated at 140 ^{o}C, 60 bar initial H_2 pressure, 0.56 catalyst/substrate wt ratio, 5h test duration and are summarized in table 1. Lower Re loadings seems to be very active towards butenes, the hydrogenation product of BD (scheme 1), nonetheless at relatively low conversion levels (entry 1-2), while the formation of 3-butene-1,2-diol is enhanced. Comparing now with entry 3, it is interesting to observe that BD is greatly favored (88% selectivity) at high conversion levels (65%). The differences in the selectivities might be attributed to the different catalyst structure obtained in each case according to XRD results. However, to avoid using high Re loadings, due to its high cost [7], the impregnation with Mo was studied at low Re loadings. From entries 4 and 5, both BD selectivity and conversion are greatly

modified revealing that impregnation with Mo contributes to maintain the C=C bond of BD due to the mild hydrogenation activity of Mo [4,5]. As both Mo-Re/BC present almost the same activity they were chosen as promising catalysts to study the evolution of erythritol HDO with reaction time.

Table 1. *Erythritol conversion & main product distribution over Re and mixed Mo-Re based catalysts at T=140 °C, $P_{in,H2}$=60 bar, catalyst/substrate=0.56 $g_{cat}/g_{erythritol}$ and t=5h.*

Entry	Catalyst	Conversion (%)	1,3-Butadiene Selectivity (%)	Butenes Selectivity (%)	3-Butene-1,2-diol Selectivity (%)
1	2Re/BC	8	-	39	57
2	5Re/BC	18	-	69	26
3	20Re/BC	65	88	5	3
4	5Mo-10Re/BC	51	93	4	4
5	10Mo-5Re/BC	39	92	2	6

Erythritol conversion and product distribution over both Mo-Re/BC as a function of reaction time are presented in figure 1. The same product trend is observed for the two materials. At short reaction times the production of 3-butene-1,2-diol, the first HDO product, is detected while by increasing the time its production becomes limited in favor of 1,3-butadiene. Increasing the reaction time up to 7h, BD is the main product detected achieving the highest selectivity (93%), while with a further increase in reaction time its production is restricted in favor of butenes and then butane. In the case of 5Mo-10Re/BC the maximum BD selectivity (93%) is achieved for 51% conversion at 5h. Comparing the activity of two materials it should be noticed that higher conversion levels are achieved over 5Mo-10Re/BC and thus, this catalyst is considered as the most promising one and is further used to study the effect of other reaction parameters.
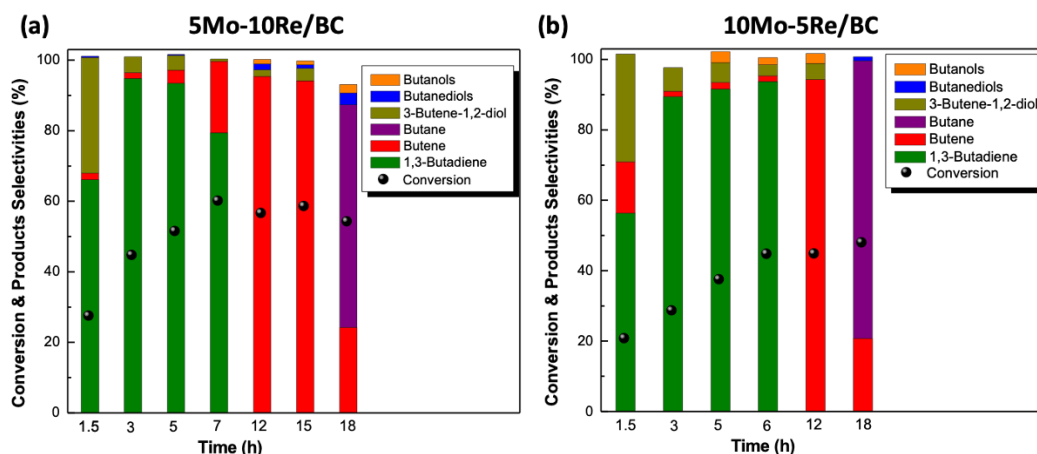
Figure 1. *Evolution of erythritol conversion and product selectivity over a)5Mo-10Re/BC and b) 10Mo-5Re/BC at T=140 °C, $P_{in,H2}$=60 bar and catalyst/substrate=0.56 $g_{cat}/g_{erythritol}$.*

The effect of reaction temperature on the catalytic performance was studied from 100 to 160 °C at constant reaction conditions ($P_{in,H2}$=60 bar, catalyst/substrate=0.56 $g_{cat}/g_{erythritol}$, t=5h). As it is expected temperature increment boosts erythritol conversion from 13% to 58%. 3-butene-1,2-diol is mostly formed at low temperatures implying that temperature does not promote the HDO step of the latter to 1,3-butadiene. The gradual temperature elevation to 140 °C highly favors BD production as it is the main product with the highest selectivity (93%). Further increase up to 160 °C, promotes butenes production (21%) along with butadiene, the selectivity of which decreased to

73%, while erythritol conversion does not remarkably change. Therefore, 140 °C was chosen as the optimum temperature. Moreover, the effect of H_2 pressure on erythritol conversion and product distribution was explored by differentiating its value from 20 to 60 bar, as well as under inert high pressure (60 bar Ar) at constant reaction conditions (T=140 °C, catalyst/substrate=0.56 $g_{cat}/g_{erythritol}$, t=5h). It was found that the effect of H_2 pressure is more pronounced on erythritol conversion compared to 1,3-butadiene production, as its value increases from 34 to 51% with increasing pressure, while in every case is the main product formed at high selectivity values (>80%). On the other hand, under inert pressure erythritol does not convert at all highlighting the important role of hydrogen in the system to produce the target product. In addition, the effect of catalyst weight was studied in the range of catalyst/substrate ratio 0.19-1.18 $g_{cat}/g_{erythrtiol}$ at constant temperature (140 °C) initial H_2 pressure (60 bar) and reaction time (5h). Although conversion increases with catalyst weight, its value does not increase proportionally implying control from mass transfer phenomena. The maximum BD selectivity (93%) is obtained at 0.56 $g_{cat}/g_{erythritol}$ for 51% conversion, while with a further increase to 1.19 $g_{cat}/g_{erythritol}$, selectivity to 1,3-butadiene decreases in favor of butenes. The sum of their selectivity values remains constant at both ratios (93%) suggesting that the increase of the catalyst active sites at the highest ratio promotes butenes production.

Effect of synthesis parameters

As 5Mo-10Re/BC catalyst presented a promising performance, the effect of calcination atmosphere and temperature was further explored. A catalyst with the same composition but calcined under oxidizing atmosphere and lower temperature 300°C was synthesized and tested under similar conditions. The catalytic results indicated that calcination atmosphere has a minor impact on erythritol conversion as it was slightly increased from 51 to 57%, while it remarkably affected product distribution. Over, 5Mo-10Re/BC_{OXID}, the hydrogenation of the C=C bond of 1,3-butadiene is promoted, as butane is the main product with the highest selectivity (60%) followed by butenes (26% selectivity). XRD graphs of the material revealed that the structure of 5Mo-10Re/BC_{OXID}, resembles that of an amorphous one suggesting that this transformation in the structure negatively affects product distribution.

In order to gain more information regarding the composition in the upper surface layer of the materials and the oxidation state of metal species, XPS measurements of fresh 5Re/BC, 5Mo-10Re/BC, 5Mo-10Re/BC_{OXID} were performed. The atomic composition in Mo and Re oxides are presented in table 2. In the case of 5Mo-10Re/BC and 5Mo-10Re/BC_{OXID} the fully oxidized Mo^{6+} species are the most abundant indicating that calcination conditions do not affect the upper surface layer of the catalyst in contrast to the bulk one, as in the case of the former the reduced species Mo^{4+} species were formed (according to XRD results). On the other hand, the population of Re species varies significantly in every case with different oxidation states coexisting on the surface. The fully oxidized Re^{6+} species are the most predominant ones. However, the fully oxidized along with the reduced species are present on the 5Re/BC and 5Mo-10Re/BC catalyst surface. The appearance of the reduced Re^{4+} species is associated with a decrease in Re^{6+} population suggesting that the applied calcination atmosphere (N_2) favors the reducibility of Re oxides in accordance with the XRD results previously mentioned. Comparing now fresh 5Mo-10Re/BC and used 5Mo-10Re/BC, the population of Re^{6+} species is decreased at half, while that of Re^{4+} remarkably increases from 7.8 to 27.1% in the used sample demonstrating that the highly reductive atmosphere during experiments favor the reduction of Re^{6+} species to Re^{4+}. It is also interesting to observed that the population of Re^{7+} species also increases from 6.1 to 28.7% in the used sample. This reduction and oxidation of Re valence on the catalyst surface indicates that most likely the HDO of erythritol proceeds via the reverse Mars van Krevelen mechanism in agreement with glycerol HDO over Mo catalysts [5].

Table 2. *XPS quantification data for population of Mo and Re at different oxidation states.*

Oxidation State	5Re/BC	5Mo-10Re/BC	5Mo-10Re/BC$_{OXID}$	Used 5Mo-10Re/BC
Mo^{6+}	-	100	100	96.40
Mo^{4+}	-	-	-	3.70
Re^{7+}	14.60	6.10	9.11	28.80
Re^{6+}	73.90	86.20	90.89	44.10
Re^{4+}	11.50	7.80		27.10

CONCLUSIONS

In this study, the activity of supported metal oxides in erythritol HDO was evaluated in liquid phase under batch conditions. Rhenium supported catalysts on black carbon exhibited a remarkable performance in terms of conversion and product selectivity and their activity is associated with catalyst structure. Low rhenium loadings (2-5%) present mostly favor the production of butenes. Re-rich catalysts with 20wt% metal loading greatly promoted 1,3-butadiene production (88%) achieving the highest conversion level 65%. Mixed Mo-Re/BC catalysts were very active in complete deoxygenation of erythritol towards butadiene with very high selectivity. It was found that 3-butene-1,2-diol is the main intermediate of the reaction, as its production is favored at short reaction times, while extended times (>5h) enhance the further hydrogenation of the target product to butenes and/or butane. Catalytic results indicated that increased temperature up to 140°C and H$_2$ pressure yp to 60bar favor both butadiene production and erythritol conversion. Under the optimum reaction conditions and over 5Mo-10Re/BC catalyst, erythritol is selectivity converted to 1,3-butadiene (51% conversion) obtaining the highest selectivity value (93%) at 140 ^{o}C, 60 bar initial H$_2$ pressure and 5h reaction time. The effect of calcination atmosphere was also studied and it was found that calcination under oxidizing atmosphere at 300 ^{o}C led to an amorphous catalyst structure promoting butane and butenes, the hydrogenation products of 1,3-butadiene. XPS measurements revealed that the surface of 5Mo-10Re/BC catalyst comprises of fully oxidized Mo^{6+} and Re^{7+}, along partially reduced Re (Re^{6+}, Re^{4+}) species the population of which changes under reaction conditions.

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