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Metal phosphate catalyzed dehydration of sorbitol under hydrothermal conditions

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ABSTRACT

The intention of this work is to develop a heterogeneously catalyzed, environmentally friendly and sustainable process for the production of isosorbide by dehydration of sorbitol. The presence of the heterogeneous catalyst BP in the batch reactor had a great influence on the reaction rate. Trivalent B-, Al-, Fe-, Ce- and La-phosphates catalysts (MeP), as well as quadrivalent Zr-phosphates (ZrP-1 and ZrP-2) were studied in liquid-phase using autoclave reactors under autogenous pressure at different temperatures between 150 and 250 °C for different reaction times between 0.5 and 24 h. The catalytic activity depends on the acidity of the catalysts, as NH_3-TPD technique revealed, on the surface area and the pore diameter determined by N_2 adsorption. Depending on the pH of the reaction medium, water molecules play a significant role in the reaction. A tremendous effect was observed when 100 wt.% sorbitol powder was used instead of aqueous 70 wt.% sorbitol solution as starting material.

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1. Introduction

Isosorbide belongs to the so-called "biomass-derived substances", obtainable from natural products, being classified as "renewable resources". This 1.4:3.6-di-anhydrohexitol is useful in the formation of numerous pharmaceutical compounds, cosmetics, products of food industry [1], as well as polymers such as polyurethane, polycarbonate, polyesters and polyamides [2,3].

An overview on catalytic sorbitol dehydration investigation has been provided by Li et al. [4], in which three research groups considering the phases of catalysts and reactants are identified. The first group claims the classic way whereby water is used as solvent for both catalysts based mineral acids and reactant [5–10]. Among the strong mineral acids (H_2SO_4, H_3PO_4, HCl) H_2SO_4 seems to be the best under the same conditions (100% sorbitol conversion and 77% isosorbide yield at 135 °C, 20 h) [10].

Recently, following a new strategy, molten $ZnCl_2$ hydrate is applied as solvent as well as catalyst. Thereby full conversion of sorbitol and high selectivity to isosorbide (>85% on molar basis) were achieved at 200 °C [4]. But besides the high pressure conditions (30 bars N_2) needed, this method presents drawbacks like all the others homogeneously catalyzed processes e.g., solvent recycle, strong salt formation [11].

The second and the third group presented more environmentally friendly and sustainable attempts by applying heterogeneous catalysts. These catalysts can be easily removed and recovered from reaction mixtures, and thus, can be used several times. Furthermore, the strong salt formation due to the neutralization of the homogeneous acid is strongly reduced and the usage of solvents and environmentally adverse chemicals are prevented [12,13]. When solid acid catalysts are used the fed sorbitol can be solid (second group, sorbitol melting point is 95 °C) or in an aqueous solution (third group).

Researchers focused on the study of using H-zeolites [14,15], SiO_2–Al_2O_3 [16], ion-exchange resins [10,17], $H_3PW_{12}O_{40}/SiO_2$ [18], anhydrous pyridinium chloride [19] and bimetallic catalysts (Cu-Pt, RANEY copper, acid promoted Pt) [20]. Acceptable yields of isosorbide (62% [16] and 81% [15]) were obtained in the presence of SiO_2–Al_2O_3 [16] and 3 Å zeolites [15], but only at elevated temperatures and pressures. Furthermore, the zeolites have the disadvantages of being expensive catalysts.

Due to the low activity and poor selectivity of classic solid acid catalysts such as silica, alumina the development of more efficient

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solid acid catalysts has been investigated. For instance, a maximum of 75% selectivity to isosorbide, with 100% conversion of sorbitol is achieved over sulfated titania at 210 °C [21].

Al-Qallaf et al. [22] described good performances of metal(IV) phosphates for selective formation of mono- and bi-cyclic ethers from diols. Metal(IV) oxides modified with H_3PO_4 [23] and metal(IV) phosphates, as tin, zirconium and titanium phosphates [24,25] were tested for selective dehydration of sorbitol to isosorbide in gas-phase. Among these quadrovalent metal phosphates tin phosphate showed the highest selectivity to isosorbide (65.4%) but with moderate sorbitol conversion (72.1%) [25]. However, these quadrovalent phosphates present the inconvenience to be expensive, because their preparation requires a sequence of energy consuming subsequent processes, e.g., calcinations, refluxing for long times, hydrothermal treatment. More than that, some of them are toxic, such the tin phosphate [26].

In recent years increasing interest has been focused on trivalent cations containing phosphates used as catalysts in organic synthesis and in petrochemical industry [27]. The Me(III) phosphates are cheaper catalysts than quadrovalent phosphate catalysts. They can be easily prepared, just by mixing together a soluble source of the trivalent metal cation and a source of the phosphate anion [28].

Sorbitol dehydration at high temperature liquid water (200–300 °C, without using any catalyst) was recently reported by Yamaguchi et al. [29], with a maximum yield of isosorbide of 55% after 3 h at 300 °C.

The objective of the present work is to develop a simple, low cost, environmentally friendly and sustainable process for the production of isosorbide by dehydration of sorbitol. Therefore this study describes investigations of the reaction carried out in liquid-phase over B-, Al-, Fe- Ce- and La- trivalent cations containing phosphates as well as the quadrovalent Zr- phosphates as catalysts under hydrothermal conditions. Although the effect of water on the dehydration of sorbitol is well known and that by continuously removing the water from the system the rate of isosorbide synthesis increases 5 times [10], in the last years the reaction has been studied in closed systems, as the batch reactors with [4] and without catalyst [29] and good results have been reported. Therefore, for comparison reasons in this paper only experiments in closed autoclaves without water separation have been carried out.

2. Experimental

2.1. Catalysts

Different metal phosphates have been studied as catalysts for sorbitol dehydration: boron phosphate (BP, kindly provided by BASF), aluminum phosphate (AlP, $AlPO_4$, CAS: 7784–30-7, bought from ABCR), two different zirconium phosphates (ZrP-1 (NZP 100) and ZrP-2 (CZP-200), both kindly sponsored by MEL), iron phosphate (FeP, $FePO_4 \cdot 4H_2O$, CAS: 31,096-47-6, bought from Fluka), lanthanum phosphate (LaP, [28,30]) and cerium phosphate (CeP, [28,30]). All these catalysts were used in the reaction as provided or as prepared or after calcination in air. BP, ZrP-1, ZrP-2 and CeP were calcined using 3 different treatments: at 200 °C for 12 h (denoted MeP^{200}), at 400 °C for 8 h (denoted MeP^{400}) and at 600 °C for 12 h (denoted MeP^{600}).

2.2. Characterization of the catalysts

X-ray diffraction (XRD) analysis was performed on a Siemens D 500 diffractometer using CuKα monochromatized radiation source operated at 40 kV and 40 mA. The BET surface area and BJH pore volumes were calculated from nitrogen adsorption/desorption at 77 K using Micromeritics ASAP 2000 instrument. NH_3-TPD was carried out with the POROTEC TPDRO 1100 instrument equipped with a thermal conductivity detector. XPS measurements were performed on a Thermo Scientific ESCALAB 250 electron spectrometer equipped with aluminum anode using the monochromatized AlKα radiation (hυ = 1486.6 eV) from an anode operated at 15 kV and 150 W. The elemental analysis was done by Inductively Coupled Plasma atomic emission spectrometry (ICP-AES) by a Spectroflame Modula FTM18 of Spectro Analytic Instrument using two monochromators in the wavelength ranges of 165–460 and 240–790 nm, respectively.

2.3. Batch reaction procedure

The batch experiments were carried out in 75 ml stainless steel autoclaves equipped with pressure gauges. The autoclave was heated up to the reaction temperature by means of an electrical heater jacket equipped with a temperature controller. The stirring was achieved using a magnetic stirring bar inside the reaction mixture. An aqueous solution with 70 wt.% sorbitol was used as reactant as well as a 100 wt.% powder (both kindly supplied by Roquette Frères, Lestrem, France). Two different amounts of reactants were tested: 25 ml/50 ml in the case of sorbitol solution and 32.3 g/45.5 g in the case of sorbitol powder, respectively. The catalyst weight was in each reaction 1 wt.% related to the amount of the sorbitol (0.32 g and 0.46 g). The autoclave was sealed and heated up to the chosen temperature and for the specified reaction time under an adjusted stirring speed (1100 rpm) and self-generated pressure. In one experiment the system was artificially pressurized to 20 bars with nitrogen gas prior to heating. After the given reaction time, the heating device was removed and the autoclave was cooled down to room temperature by immersing into an ice bath. Six different temperatures were adjusted at 150, 180, 190, 200, 220 and 250 °C for different reaction times of 0.5, 1, 2, 4, 8, 12 and 24 h.

2.4. Gas chromatography

The gas chromatographic analysis was performed on a Hewlett Packard HP 6890 Series GC system, using a capillary column FS-OV-1-CB, CS25208-1 (50 m × 0.25 μm × 0.25 μm). The temperature program of the column was: 140 °C, 2°/min, 250 °C. The injected volume was: 1 μl.

The GC samples were prepared as follows. Around 100 mg of sample (the mixture obtained at the end of the reaction) was solved in 1 ml pyridine. This solution was called 'concentrated solution'. A big volume of a solution of ethylene glycol (used as internal standard, IS) was prepared as follows: 3.1214 g of ethylene glycol were solved in 50 ml pyridine. From this solution 0.67 ml were taken for each analysis. These 0.67 ml of IS solution were mixed with 2 ml of *N,O*-bis(trimethylsilyl) trifluoroacetamide with 1% trimethylchlorosilane (BSTFA + 1% TMCS, reagent for trimethylsilylation). This new solution was called 'silylation solution'. 0.1 ml of 'concentrated solution' was mixed with 0.8 ml of 'silylation solution'. The mixing process was performed in ultrasound batch for 30 min. So, for silylation of the sample it was used the following rapport: 6 mg sample/5 mg IS/2 ml BSTFA.

For the calculations of conversion and selectivities the total mass of the sample analyzed was considered equal with the initial mass of the reactant. The conversion of sorbitol was determined from the percentage of transformed sorbitol (sorbitol initial – sorbitol in the sample).

$$X_{SORBITOL} = \frac{m_{S\ ORBITOL\ INITIAL} - \%_{SORBITOL}/100 \times m_{TOTAL\ SAMPLE}}{m_{SORBITOL\ INITIAL}} \times 100, \text{ where}$$

$X_{SORBITOL}$ is conversion of sorbitol, % mol, $m_{SORBITOL\ INITIAL}$ is the initial mass of sorbitol, g, $\%_{SORBITOL}$ is the % of sorbitol determined by GC in the sample analyzed,