Catalysis Communications 13 (2011) 1–5

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Tuning selectivity of $Pt/CaCO_3$ in glycerol hydrogenolysis — A Design of Experiments approach

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ARTICLE INFO

Article history:
Received 18 March 2011
Received in revised form 25 May 2011
Accepted 6 June 2011
Available online 13 June 2011

Keywords:
Design of Experiment
Heterogeneous catalysis
Glycerol
Boric acid
1,2-propanediol
Lactic acid

ABSTRACT

19 commercially available catalysts have been effectively screened in only 30 experiments for the hydrogenolysis of glycerol using a D-optimal design. $Pt/CaCO_3$ emerged as both an active and selective catalyst and was studied in greater detail using a Central Composite Design. Upon addition of boric acid, the $Pt/CaCO_3$ product selectivity could be changed from 1,2-propanediol towards lactic acid. The formation of 1,2-propanediol and lactic acid could be optimized by considering the Response Surface Model plots and formation pathways.

1. Introduction

The production of chemicals from biomass is an essential feature of a sustainable future [1,2]. Polyols and sugars constitute a considerable fraction of the available biomass and are therefore an attractive feedstock for bio-based chemicals [3,4]. These oxygen rich starting materials need to be defunctionalized to produce appropriate building blocks for the chemical industry. Hydrogenolysis is a key process to achieve this goal [5].

Glycerol is an attractive starting material for hydrogenolysis, since it can serve as a model compound for larger polyols and sugars [6]. The added advantage is the economical relevance of its conversion into 1,2-propanediol (12PD) and 1,3-propanediol (13PD), both used in polymer synthesis [7]. Interestingly, glycerol can also yield lactic acid (LA), an oxidation product, under hydrogenolysis conditions [8,9]. This base-induced reaction resembles an intra-molecular Cannizzaro reaction and needs to be taken into consideration in the overall process (Scheme 1) [10].

The aim of this research is to identify a selective catalyst for the hydrogenolysis of glycerol in water, and to achieve a better understanding of the variables influencing its activity and selectivity. Furthermore, we envision the influence of boric acid (BA) on selectivity of catalysts in the hydrogenolysis reaction of glycerol through formation of borate esters in solution, and thereby, leaving a single hydroxyl group accessible for dehydrogenation (Scheme 2) [11].

Numerous papers describe the formation of 12PD through hydrogenolysis of glycerol, employing different catalysts and conditions [12–19]. This led to a general picture of the formation of 12PD. Still, the effect of individual variables is not completely understood. This is where a method such as Design of Experiments (DoE) can be very efficient to readily determine the influence of several variables on activity and selectivity of the catalysts, and elucidate the effects of BA [20].

2. Experimental

Full details are given in the Supplementary Data.

2.1. Reaction procedure

Standard reaction mixtures were prepared by dissolving appropriate amounts of glycerol and BA in demineralized water in the volumetric flask adjusting the pH with 0.1 M aqueous sodium hydroxide (Tables S1 and S2, Supplementary Data).

The hydrogenolysis of glycerol was performed in a HEL PolyBLOCK 8, a parallel autoclave reactor system consisting of eight 16 mL vessels. The appropriate amount of catalyst (5 mol% active metal, relative to glycerol) was added to 5 mL of aqueous standard reaction mixture. Reactors were purged 3 times with N_2 (20 bar) and 3 times with H_2 (40 bar). Then they were pressurized to 40 bar H_2, stirred at 800 rpm and heated to the reaction temperature within 20 min. Stirring was

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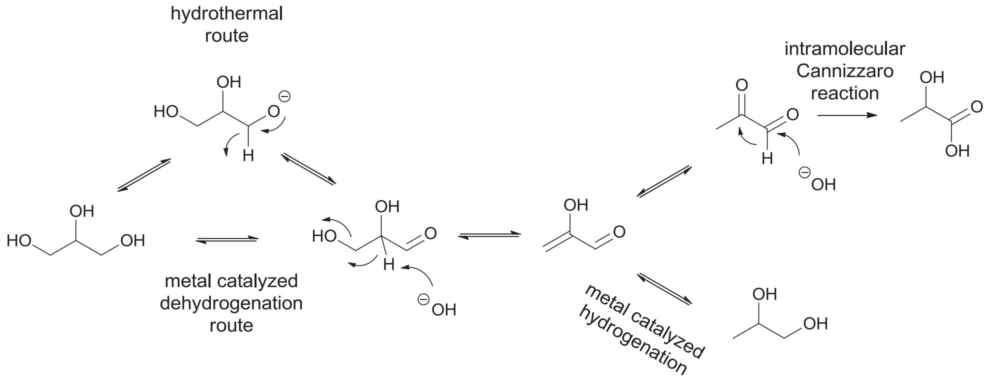
doi:10.1016/j.catcom.2011.06.007



Scheme 1. The formation pathway of 12PD and LA from glycerol.

stopped after 18 h and the reactors were allowed to cool down to room temperature. Then the reaction mixture was filtered over a nylon micro filter (Rotilabo, 0.2 μm). An HPLC sample was prepared by diluting 500 μL filtered reaction mixture using 500 μL 5 mM H_2SO_4. The liquid products were analyzed by HPLC. Products detected by HPLC were 12PD, LA, EG and EtOH [21].

3. Results and discussion

3.1. D-optimal design

A series of variables (temperature, pH, additive) and 19 heterogeneous catalysts, with comparable porosity and surface area within each support class (Table 1), were screened for hydrogenolysis activity, using a DoE approach to optimize the experimental effort. Temperature was chosen for its expected influence on the conversion of glycerol, while the effect of pH influences the equilibrium reaction of glycerol with BA and can therefore affect the overall reaction as well. Sulfolane has been shown to have an influence on reaction selectivity and was therefore included in this initial screening [11].

Factorial designs or fractional factorial designs can be used in case of screening of continuous variables, such as pH and temperature. However, in this case some of the variables are discrete (active metal and support type), for which a D-optimal design is more efficient. This is due to the fact that a complete factorial is needed for every combination of discrete variables, which hugely increases the experimental effort. The aim of the initial D-optimal screenings was to evaluate the main influence of the individual variables, which results in a minimal amount of experiments. For this reason the amount of continuous variables was limited to three. The design will result in a model by fitting the experimental data in a polynomial, which will only describe the main variables in the form of a first order polynomial (Eq. (1)).

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \varepsilon \qquad (1)$$

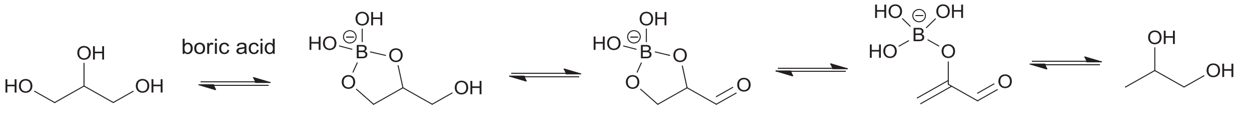
Here, y is the response (in this case glycerol conversion), x_i is variable i, β_0 is the intercept and β_i is the coefficient of variable i and ε includes the experimental error and the effects of any uncontrolled variable present. This initial result allows for choosing an appropriate catalyst, which can be optimized in a subsequent, more detailed study.

We envisioned that BA could influence the selectivity of the hydrogenolysis by forming borate esters in solution. Borate esters are only formed at alkaline pH [22]. Therefore, the pH values were varied between 10 and 12. Preliminary experiments showed that hydrogenolysis occurs at temperatures between 150 and 200 °C. The effect of sulfolane as an additive was investigated, because earlier research had demonstrated that this polar, aprotic solvent could affect the selectivity of several catalysts [11,23].

The catalysts were divided into two groups and a D-optimal design was constructed for both. Design 1 was used to screen 15 catalysts, considering the variables: active metal (Ni, Pd, Pt, Rh, Ru), support type (Al_2O_3, C, SiO_2), temperature (150–200 °C), pH (9–12) and additive (0–5% v/v sulfolane). Design 2 was employed to screen the remaining four catalysts (Ir/C, Pd/$BaSO_4$, Pd/$CaCO_3$, Pt/$CaCO_3$) and the same three continuous variables. The division of the catalysts in these two groups was done since not all the combinations of active metal and support type were available. Thus, using these two designs, 19 catalysts could be effectively screened in only 30, out of a total of 240, experiments (Table S1, Supplementary Data).

It appeared that the Ru catalysts in design 1 were especially active. However, they mainly degraded the glycerol and only small amounts of C3 products were detected. Due to the setup of our parallel autoclaves (no option for sampling over time) we could not compare catalyst selectivities at comparable conversions. The reaction products are prone to further degradation. Therefore, the performance of the Ru catalysts will probably be improved when the reaction is stopped before 18 h. Therefore, the ruthenium catalysts were excluded from the dataset for polynomial fitting. This resulted in a statistical polynomial model, of which the significant coefficients are plotted in the coefficient plot regarding the glycerol conversion (Figure S1a). It shows that only the variables active metal, support type and temperature have a significant influence on glycerol conversion. In this case the additive and pH had no significant influence on glycerol conversion and are therefore not included in the coefficient plot.

In design 2, the Pd/$CaCO_3$ catalyst appeared to be not active at all. By excluding the three Pd/$CaCO_3$ experiments, the total number of



Scheme 2. BA as a hypothetical selectivity inducer through the formation of borate esters.

Table 1
Porosity and BET surface area of catalysts.

Catalyst	Metal loading (wt.%)	V_{pore} (mL/g)	S_{BET} (m^2/g)
Ni/Al_2O_3[a]	50	0.52	209
Pd/Al_2O_3[a]	5	0.24	171
Pt/Al_2O_3[a]	5	0.44	212
Rh/Al_2O_3[a]	5	0.40	150
Ru/Al_2O_3[a]	5	0.38	100
Ni/C[a]	75	0.34	803
Pd/C[a]	5	0.70	951
Pt/C[a]	5	0.68	1010
Rh/C[a]	5	0.77	985
Ru/C[a]	5	0.54	839
Ir/C[b]	5	0.57	954
Ni/SiO_2[a]	66	0.17	104
Pd/SiO_2[a]	5	1.00	221
Pt/SiO_2[a]	1	1.03	236
Rh/SiO_2[a]	5	0.95	247
Ru/SiO_2[a]	5	0.99	324
$Pd/BaSO_4$[b]	5	0.03	10
$Pd/CaCO_3$[b]	5	0.03	8
$Pt/CaCO_3$[b]	5	0.04	11

[a] Used in D-optimal design 1.
[b] Used in D-optimal design 2.

catalysts was reduced from four to three and the results could be correlated by a polynomial model. The coefficients of this model are plotted in the coefficient plot regarding the glycerol conversion (Figure S1b). This model showed that in addition to the catalysts, temperature and the presence of sulfolane influence the conversion of glycerol, with a large positive and a small negative effect, respectively. pH had no significant effect on glycerol conversion and was therefore omitted from the coefficient plot.

3.2. LA formation

It is remarkable that an oxidation product such as LA can be formed under reductive hydrogenolysis conditions. Its hydrothermal formation from glycerol in the absence of a metal (95% conversion, 90% selectivity, Scheme 1) was reported by Kishida et al. [24]. However, 300 °C was required to overcome the energy barrier raised by the hydride elimination. Maris et al. reported the formation of LA at a relatively reduced temperature (200 °C) in the presence of heterogeneous catalysts (Pt/C, Ru/C, AuRu/C or PtRu/C) [8]. Apparently, the addition of a catalyst could lower the reaction temperature. This can be explained by the presence of a metallic surface, facilitating the dehydrogenation of a hydroxyl group. To exclude that boric acid is sufficient to catalyze the LA formation, a blank experiment was performed in the absence of catalyst. This showed only 0.5% LA formation, confirming the catalytic role of the metal catalyst.

3.3. Influence of BA on activity and selectivity

Our initial hypothesis was that BA could influence the selectivity of the hydrogenolysis through formation of borate esters in solution, leaving one hydroxyl group available for reduction. As a Lewis acid, BA can also activate the hydroxyl groups of glycerol and increase the activity.

The effect of BA on the activity and selectivity of the catalysts was investigated by repeating a set of six successful experiments from the two D-optimal designs, this time in the absence of BA (Fig. 1). This showed that in most cases, the activity is increased upon addition of BA (Fig. 1a); in the case of $Pt/CaCO_3$ the activity is even more than doubled.

Not only conversion of glycerol was increased (in most cases) in the presence of BA, also less glycerol was degraded (Fig. 1b). Consequently, more glycerol is converted into desired products, best expressed for

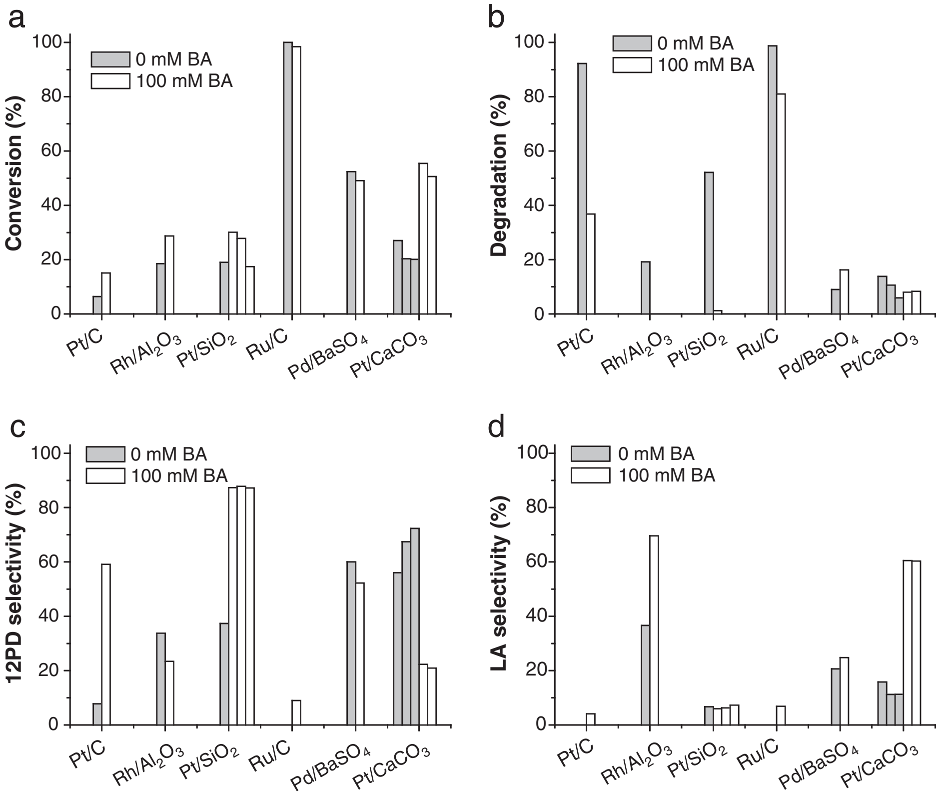


Fig. 1. The influence of BA on [a] conversion; [b] degradation; [c] 12PD-selectivity and [d] LA selectivity. Some reactions were performed in duplicate or triplicate in order to establish the error margin. Reaction conditions for the respective catalysts are given in Table S1, Supplementary Data.

Rh/Al_2O_3 and Pt/SiO_2, where the degradation of glycerol is almost completely suppressed.

Interestingly, BA's influence on selectivity is not clear-cut. In some cases (Pt/C, Pt/SiO_2) 12PD-selectivity was substantially increased (Fig. 1c), while in other cases (Rh/Al_2O_3, $Pt/CaCO_3$) LA formation was favored upon the addition of BA (Fig. 1d). In case of $Pt/CaCO_3$ the increase of LA-selectivity was accompanied by a decrease of 12PD-selectivity, resulting in a selectivity switch from 12PD to LA upon the addition of BA.

3.4. Response Surface Model design

A Central Composite Design (CCD) was set up to study the significant influence of BA on the selectivity of $Pt/CaCO_3$. A CCD consists of a full factorial design augmented with star points, which increase the variable space and allow the modeling of nonlinear effects. A CCD results in a Response Surface Model (RSM), which enables to draw insightful RSM plots (Fig. 2, raw data in Table S2, Supplementary Data).

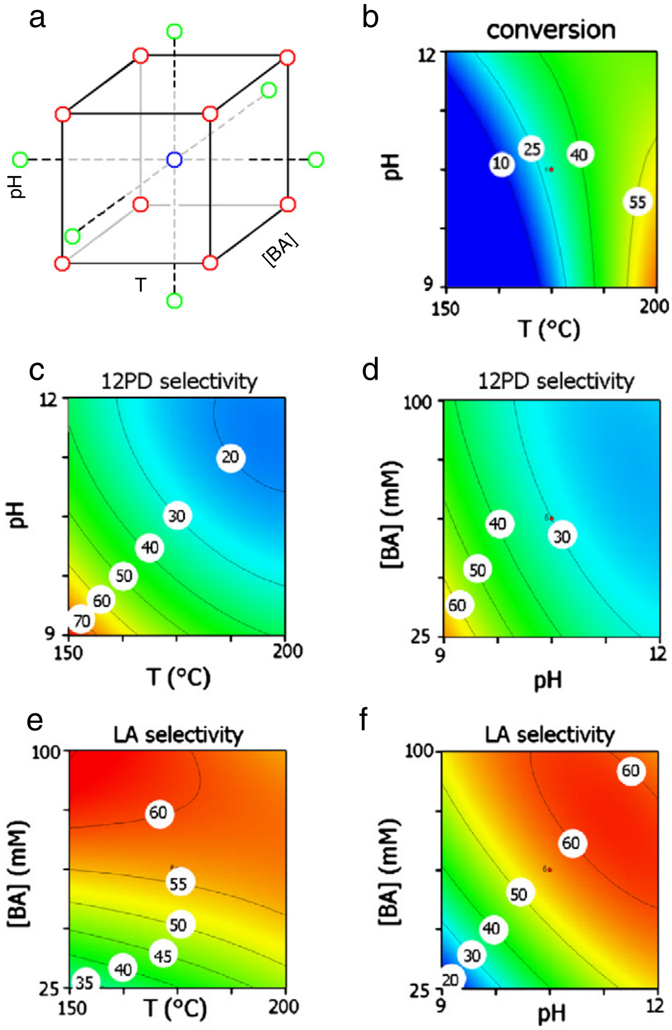


Fig. 2. RSM-plots resulting from a Central Composite Design. Relevant cross sections through the center points were chosen and the value of the remaining parameter is given in the respective footnote. [a] Central Composite Design, the circles represent experiments within parameter space, blue = 6 × center point, red = 8 × factorial point, green = 6 × star point; [b] RSM-plot for glycerol conversion at 62.5 mM BA; [c] RSM-plot for 12PD-selectivity at 62.5 mM BA; [d] RSM-plot for 12PD-selectivity at 175 °C; [e] RSM-plot for LA-selectivity at pH 10.5; [f] RSM-plot for LA-selectivity at 175 °C.

In addition to BA concentration (0–125 mM), the influence of the variables temperature (130–220 °C) and pH (8–13) on activity and selectivity of the catalyst were investigated. These three variables could be effectively modeled using a CCD consisting of 20 experiments (8 factorial points, 6 star points and 6 center points) (Fig. 2a). The center point is repeated six times in order to obtain a good estimate for the standard deviation of the system. The model for the conversion of glycerol indicated that the variable temperature and the interaction pH × temperature have a significant effect on the conversion of glycerol. These effects are visualized in the RSM plot in Fig. 2b: pH has an influence on glycerol conversion, but it is mainly controlled by temperature.

The selectivity of $Pt/CaCO_3$ towards 12PD and LA was modeled by omitting the selectivity data at conversions below 5%. These data were excluded because the low conversion data contain a high uncertainty in the selectivity. The resulting selectivity models show an influence of all three variables, best visualized in RSM plots (Fig. 2c–f).

The selectivity, within variable space, towards 12PD is highest at low BA concentration, low pH and low temperature (Fig. 2c–d). However, at these conditions the conversion of glycerol is very low, resulting in the formation of a small amount of 12PD.

The LA-selectivity is the highest at high pH and BA concentration, while the effect of temperature is less significant (Fig. 2e–f). This means that a high LA-selectivity is possible at a relatively high glycerol conversion. Interestingly, it is visualized that upon changing reaction variables, $Pt/CaCO_3$ can be either selective for 12PD or LA formation.

3.5. Increasing 12PD-selectivity

Based on the RSM plots in Fig. 2(c and d), it can be expected that decreasing pH below pH 9 at 200 °C should increase 12PD-selectivity, while maintaining a high conversion. Therefore, an additional reaction was run at 200 °C, 100 mM BA concentration and pH 5.6, i.e. without addition of sodium hydroxide (Fig. 3a). Indeed, this resulted in a substantial increase of 12PD-selectivity, accompanied by a decimation of the LA-selectivity. The overall yield of 12PD was increased, even though the glycerol conversion was decreased. Mechanistically, the increase in 12PD-selectivity can be explained by the suppression of the LA formation pathway, since this is base-induced [23], leaving more glycerol for hydrogenolysis to 12PD. A reason for the decrease of conversion rate could be that at pH 5.6 only one pathway is operational, instead of two pathways at pH 12.

3.6. Increasing LA-formation

The RSM plots show that an optimum for LA-selectivity is close to, or within the chosen parameter space (Fig. 2e–f). Therefore, changing these variables would not substantially increase the LA-selectivity. However, the selectivity could be increased by avoiding the 12PD formation pathway. This can be achieved by running the reaction in the absence of hydrogen, thereby prohibiting the formation of 12PD and leaving the dehydrogenated glycerol available for LA formation. Fig. 3b shows that in the absence of hydrogen pressure, the LA-selectivity remains the same, while the conversion and, as a consequence, the LA-formation were substantially increased. The 12PD-selectivity had dropped considerably, but still small amounts of 12PD were formed. Obviously, hydrogen, necessary for 12PD formation, is produced during the reaction: one equivalent of hydrogen is formed for each LA and even more can be formed during the degradation of glycerol [18].

3.7. Catalyst recycling

The carrier material of $Pt/CaCO_3$ should be stable under the alkaline conditions used in this study. However, the elevated temperatures and stirring might degrade the catalyst to some extent. Therefore, the

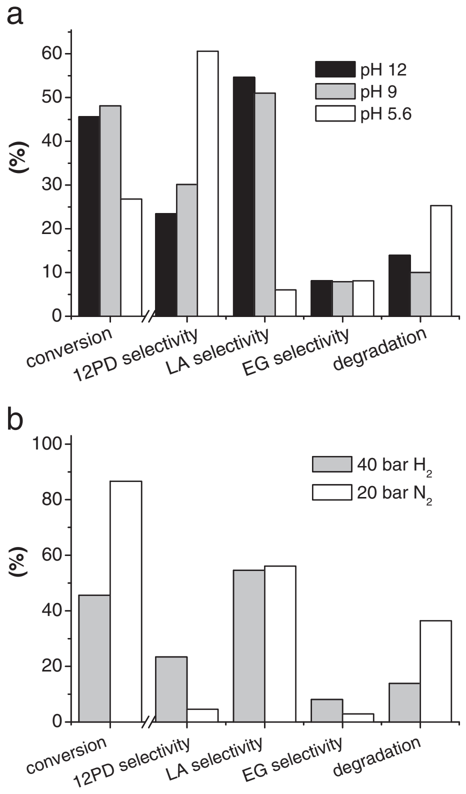


Fig. 3. [a] Effect of pH on glycerol conversion and selectivity. Reaction conditions: 5 mol% Pt/$CaCO_3$, 5 mL aqueous reaction mixture (100 mM glycerol, 100 mM BA, variable pH), 200 °C, 40 bar H_2, 18 h, 800 rpm; [b] Effect of hydrogen pressure vs. inert atmosphere. Reaction conditions: 5 mol% Pt/$CaCO_3$, 5 mL aqueous reaction mixture (100 mM glycerol, 100 mM BA, pH 12), 200 °C, 40 bar H_2 or 20 bar N_2, 18 h, 800 rpm.

stability of Pt/$CaCO_3$ was investigated by means of a catalyst recycling experiment (Figure S2, Supplemental Data).[1]

The selectivity of recycled catalyst is comparable with the selectivity of fresh catalyst, but the activity decreased when using the recycled catalyst. TEM analysis before and after reaction (Figure S3, Supplementary Data) shows that the $CaCO_3$ surface is partly eroded and platinum particles have sintered. The resulting loss of active sites can explain the lower catalyst activity.

4. Conclusions

The D-optimal screening of 19 catalysts showed that active metal, catalyst support and temperature have the highest influence on glycerol hydrogenolysis activity. A preliminary study regarding the effect of BA indicated that it can increase glycerol conversion and influences selectivity of the catalysts. Upon addition of BA, the selectivity of Pt/$CaCO_3$ was switched from 12PD to LA. Among all catalysts screened in the D-optimal design, Pt/$CaCO_3$ was found to be the most active with little glycerol degradation. A Central Composite Design revealed the strong relation between the pH and 12PD-selectivity. Decreasing the pH gave higher 12PD-selectivity by suppressing the base catalyzed LA formation pathway. Performing the reaction in the absence of hydrogen increased the LA formation due to interruption of the 12PD formation. Although LA-selectivity remained the same, conversion was considerably increased, while 12PD-selectivity was diminished. The catalyst could be recycled and maintained selectivity, but showed some deactivation.

This study shows that DoE was not only highly effective in identifying active catalysts, it also provided useful insights into the effects of pH, BA concentration and temperature on the activity and selectivity of the selected Pt/$CaCO_3$. These insights were successfully used to direct the selectivity of Pt/$CaCO_3$ to either 12PD or LA.

Acknowledgments

We are grateful to Dr. Silvia Pereira for assistance regarding DoE and to Dr. Catherine Pinel (IRCELYON) for helping us with the HPLC analysis. Jeroen ten Dam gratefully acknowledges financial support from NWO ASPECT (053.62.020).

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.06.007.

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[1] For the recycling study a new batch of catalyst has been used. The new batch had higher activity and comparable selectivities.