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Fully integrated high-throughput methodology for the study of Ni- and Cu-supported catalysts for glucose hydrogenation

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Abstract: A high-throughput (HT) methodology was applied for the synthesis, characterization and catalytic testing of silica and alumina supported Cu- and Ni-based catalysts for glucose hydrogenation. A design of Experiment (DoE) approach was also used in all steps. The deposition and reduction of both metals was performed using the chemical reduction with hydrazine method. In total, 36 catalysts were synthetized, characterized and tested in 5 days. The amount of metal deposited on the support was chosen as the discriminative and determining parameter. The catalysts were tested at low temperature (130°C) in the hydrogenation of glucose to sorbitol. The results showed that the chemical reduction-precipitation method could be performed using fully automatized robots. The deposition of the metals strongly depended on the nature of the support, the temperature of the reduction and hydrazine/H_2O ratio. The maximum metal precipitation occurred at higher temperature (70°C) and lower N_2H_4/H_2O ratio (0.04 mol/mol) in both cases. The results clearly showed that glucose conversion is higher for the catalysts synthesized at 70°C compared to the catalysts synthesized at 50°C, irrespective of the metal precursors, supports and hydrazine/water ratios employed during catalysts syntheses. With a total timespan of around 5 days we showed that HT methods applied to all the steps (synthesis, characterization and testing) can significantly reduce the time needed to develop a new catalytic process.

Keywords: high-throughput, design of experiments, heterogeneous catalysis, XRF, hydrogenation, glucose, sorbitol, biomass.

Highlights:

- High-throughput methods allow shortening the time of development of a new catalytic process
- Ni and Cu-supported catalysts can be easily obtained by reduction-precipitation method
- The activity strongly depends on preparation conditions
- The use of Design of Experiments (DoE) permits to minimize the number of experiments and to optimize their interpretation
- Good performances in hydrogenation of glucose to sorbitol were obtained for Cu/SiO_2 and Ni/Al_2O_3 catalysts

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1. Introduction

The industrial use of catalysis is increasing day by day as it is also extensively used in the constantly growing chemical and petroleum industries. Recently, trends in biomass conversion catalysis have flourished, as there is an increasing demand for the technologies based on the production of renewable energy and chemicals. Despite of the increasing research on biomass catalysis in the laboratories worldwide, the industrialization of developed processes lag behind especially due to the large amount of time, energy and money needed for the up-scaling. High-throughput (HT) approach acts as a mediator between the laboratories and the industries that are keen to develop novel processes in the areas of biomass catalysis thereby reducing the time, energy and money constraints [1]. Since glucose is one of the most common and readily available biomass primary compounds, we demonstrate in this study the use of high-throughput approach to synthesize, characterize and test Ni- and Cu-based catalysts for the hydrogenation of glucose.

Hydrogenation of glucose to sorbitol has been gaining importance since past decades, not only because sorbitol is one of the main target chemicals produced from renewable biomass but also due to its widespread use in industries like pharma, cosmetic and polymers [2]. Various catalysts based on nickel, cobalt, ruthenium, platinum and palladium have been so far employed for the hydrogenation of glucose [2 - 6]. The most common solid catalysts used for sugar hydrogenation to sugar alcohols in industrial scale are based on nickel, such as Raney nickel, but the use of ruthenium is also reported, since Ru showed a good activity and an excellent selectivity [4, 7 - 9]. The main problem when working with these kinds of catalysts is their rapid deactivation due to the metal leaching, metal sintering, and support degradation. For example in the case of industrial Ru/Al_2O_3 catalyst deactivation due to the poisoning by sulfur compounds and deposition of iron atoms leaching from industrial reactor walls was observed [10 - 11]. In the case of another industrial catalyst such as 5% Ru/C, a lost of 25% of its initial activity was observed due to the deposition of organic impurities on the catalyst surface [12]. Typically, the selectivity towards the sugar alcohol is high, exceeding 95% under optimal conditions [13 - 15]. In some special cases, such as hydrogenation of fructose to mannitol, the product selectivity is a big issue; the best selectivities of mannitol are limited to about 60-70% on Cu-based catalysts, the by-product being sorbitol [16]. Though, Raney-Ni catalysts are typically employed in the industrial production of sorbitol due to its low cost, Ni catalyst underwent leaching of active Ni into reaction mixture thereby increasing the cost of purification. Hence, numerous research studies have been conducted to develop catalysts, especially based on Ni, by varying synthesis methodologies, metal precursors, supports, particle size and promoters [5, 17]. These developments and optimizations for novel catalysts that will be cheap and efficient for the hydrogenation of glucose are time and money consuming, thereby increasing the time lag to move the process from the laboratory to the industrial scale. In this study, we carried out High-Throughput (HT) experiments combined with a Design of Experiments (DoE) methodology to perform syntheses, characterizations and testing of Ni- and Cu- based catalysts supported on SiO_2 and Al_2O_3. We demonstrated that this combination of HT experiments and DoE methodology enables a significant time, energy and money savings in the development of an optimal glucose hydrogenation to sorbitol catalysts.

2. Experimental

2.1. Catalysts preparation

2.1.1 High-throughput equipment used for synthesis

The metal precursors used for the catalysts preparation were nickel (II) nitrate (99.0%, Fluka) and copper (II) nitrate (99.0%, Sigma Aldrich). SiO_2 and γ-Al_2O_3 supports were supplied by Cariact (150 - 500 µm, BET surface area of 210 $m^2.g^{-1}$) and Sigma Aldrich (RQ10, 105µm, BET surface area of 190 $m^2.g^{-1}$), respectively. Hydrazine hydrate containing 24-26% water solution purchased from Fluka was used as the reductant. Catalysts based on nickel and copper supported on silica/alumina were prepared by the reduction of metal (II) salts with hydrazine in aqueous medium, as proposed by Wojcieszak *et al.* [18 - 19]. In an inert atmosphere, hydrazine allows reduction and precipitation of Ni and Cu metals according to the following reaction:

$$M^{2+}(aq) + N_2H_4(aq) + 2\ OH^-(aq) \rightarrow M^0(s) + N_2(g) + H_2(g) + 2\ H_2O(aq) \text{ with M= Ni or Cu}$$

After reduction, the obtained solid was filtered off, washed with distilled water and dried at 100°C to obtain the final catalyst. Synthesis of the monometallic Ni and Cu catalysts supported on Al_2O_3 and SiO_2 were performed on a Chemspeed Catimpreg workstation (Figure 1), located in the REALCAT platform, that is mainly designed to perform automated parallel synthesis of catalysts by precipitation, co-precipitation and impregnation methods [20 - 22]. The detailed description of the HT catalyst synthesis using Catimpreg workstation is given below.



Figure 1. The Chemspeed Catimpreg workstation used for catalysts preparation comprising **(a)** 4 Needles-Head (4 NH), **(b)** Gravimetric Dispensing Unit for Viscous solution (GDU-V), **(c)** Isynth reactors blocks, **(d)** Solid Dispensing Unit (SDU), **(e)** Screw capper and **(f)** Multigripper

ISynth reactor blocks (Figure 1c) were designed to carry out parallel synthesis of 24 catalysts. It consists of 24 disposable reactors each with the capacity of 20mL, an array cover plate and an orbital

shaking system. Opening and closure of the reactors are controlled by a Mutigripper unit (Figure 1f) that controls the three ceramic drawers attached to the reactor blocks. Each drawer is connected to a 3/2-way valve that aid in setting each reactor columns to either vacuum or inert gas atmosphere. The ISynth reactor blocks are also equipped with a fluid cooling/heating option that provides temperature control from -10 °C to 150°C via a circulating heat transfer fluid and a reflux plate. The distribution of solid Al_2O_3 and SiO_2 powders was performed automatically using the Solid Dispensing Unit (SDU) (Figure 1d), comprising an overhead balance with a resolution of 0.50 mg. It allowed the dispensing and weighing of the powders into various reactor vials. The gravimetrical Dispensing Unit (GDU-V, Figure 1b) was used to perform automated, gravimetrically controlled dispenses of aqueous Ni and Cu nitrate solutions. The GDU-V includes an overhead analytical balance with a readability of 1.0 mg and is equipped with an automated device for the uptake of positive displacement disposable syringes, hence allowing aspiration, dispensing and simultaneous weighing of the liquids into different reactor blocks. The 4 Needles-Head (4NH) tool (Figure 1a) equipped with four equally expandable needles was used for volumetric distribution of the hydrazine/water mixture. The ScrewCapper (Figure 1e) is the tool used to transport, close or open the caps of reactor vials containing hydrazine/water mixture and Cu/Ni nitrate solutions before their distribution.

2.1.2 Catalysts synthesis protocols

Before starting the HT synthesis, the workstation was installed with: the containers with SiO_2 and Al_2O_3 powders, the bottles (capacity of 1 L) containing pure water for synthesis and cleaning of the needles (4-NH), the 8 mL vials with Cu or Ni nitrates solution and with N_2H_4/water solution. All the syringes and 4-NH needles were automatically purged and cleaned. The reactors on the Isynth blocks were heated up to 20°C followed by reflux. After the distribution of appropriate quantity of supports and metal precursors in the reactors, the system was closed and stirred at 400 RPM for 5 minutes. Then, after decreasing the stirring speed to 200 RPM, the reactors drawers were opened and N_2H_4/water solution (concentration varied according to the experimental plan, see section 2.1.3) was added drop by drop into the reactors. Then, the reactors were closed before continuing the agitation (400 RPM) and heating during 2 hours (final temperature varied according to the experimental plan, see section 2.1.3). The precipitation step was followed by automatic filtration to eliminate the liquids. After cooling the system the liquids inside the reactors were evacuated by aspiration using vacuum pump for 5 minutes. The dried solids were washed using 10 mL of water. The reactor vials were then closed and agitated at 400 RPM for 5 minutes. The solution after washing was eliminated by aspiration using vacuum as aforementioned. The washing step was repeated thrice to completely remove any left-over hydrazine and precursor residues in the catalysts. The catalysts were then dried by heating the reactors at 100 °C for 1h along with the aspiration by vacuum pump (600 mbar) to evacuate the vapors completely from the reactors. Finally, the temperature of Isynth reactors was cooled down to 20°C and the vacuum pump and agitation process were stopped. The catalysts are designated by (wt% metal precursor)/(support) - temperature °C - (N_2H_4/H_2O ratio), that are used during the time of synthesis. For example, 5%Ni/Al_2O_3 - 70°C-0.17 is the designation of the alumina supported catalyst where 5wt.% of nickel was loaded at a temperature of 70°C and using N_2H_4/H_2O molar ratio of 0.17.

2.1.3 Design of Experiments for catalysts synthesis

The objectives of this experimental design were to obtain the most favorable conditions for the deposition of Ni or Cu on SiO_2 or Al_2O_3 by the reduction-precipitation method and to evaluate simultaneously the influence of five different factors i) precursor types (Ni or Cu nitrate), ii) precursor quantities (i.e. metal loading), iii) nature of the support (SiO_2 *vs* Al_2O_3), iv) temperature of the reduction and v) N_2H_4/H_2O molar ratio. A design of experiments (DoE) was applied to evaluate the influence of the aforementioned parameters on the catalysts syntheses. Firstly, a full factorial design (FFD) was used with five factors at two levels of evaluation (low (-1) and high (+1)) and central level (0) to evaluate the error of the DoE model (Table 1). The aforementioned "levels" are used in FFD to easily represent the minimum, the central and the maximum values of a factor influencing the synthesis. In FFD, all the possible combinations of high and low levels are studied for all five factors. Hence, the total number of conditions (or syntheses) for the fractional factorial design was 32 as calculated by 2^n (n = 5, the number of factors in this study and 2 is the number of levels). As the "support" and the "precursor type" are non-numerical factors, no zero level can be applied for these two parameters. Therefore, only a total of four central experiments could be performed by varying the possible non-numerical parameters (two supports and two precursor types) around the three numerical parameters that are fixed at zero level (Table 2). Thus, considering the five different factors employed in our study, the total numbers of possible experiments (or syntheses) were 36 (32+ 4 respectively) (see Table S1 in supporting information).

Table 1. Five factors and their levels used in the factorial design

Factor	Level -1	Level 0	Level +1
Support	SiO_2	-	Al_2O_3
Precursor amount (wt.%)	1%	3%	5%
Precursor type	Copper (II) nitrate	-	Nickel (II) nitrate
Temperature (°C)	50	60	70
N_2H_4/H_2O molar ratio	0.04	0.11	0.17

Further, the "response variable" was used in order to evaluate the most influential parameter/condition for depositing a maximal amount of metal onto the support during the syntheses. This "response variable" was the ratio of the quantity of effectively precipitated metal, which is determined by the XRF analysis, to the theoretical quantity (i.e. 1, 3 or 5 wt.%). All syntheses have been repeated twice and the results indicated that the values were reproducible. Hence, for each experiment a mean value of the two syntheses was used in the DoE.

Table 2. Four central levels experiments used in the factorial DoE

Precursor type	Support	Temperature (°C)	Precursor amount (%)	N_2H_4/H_2O
Nickel (II) nitrate	Al_2O_3	60	3	0.11
Nickel (II) nitrate	SiO_2	60	3	0.11
Copper(II) nitrate	Al_2O_3	60	3	0.11
Copper(II) nitrate	SiO_2	60	3	0.11

The DoE matrix was then established and processed using the Minitab® software. The effects and significance of the factors and their 3rd order factor interactions were evaluated using Pareto's chart. Finally, the significance of the effects and probability of random error were then estimated by analyzing the variance (ANOVA) and using the p-value significance levels.

2.2. Characterizations of catalysts

Powder X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance powder X-ray diffractometer equipped with a Cu Kα1 radiation source (λ=0.1538 nm) operating at 40 kV/40 mA and a detector 1D Lynx eyes. The diffraction intensities were measured over a 2θ range of 10 - 70° with a step size of 0.014° and a count time of 0.1 s per step. Reference data from ICDD files were used in the identification of crystalline phases.

Scanning electron microscopy (SEM) of the solids was performed on a Hitachi-S3600N instrument employed with a Thermo UltraDry detector operating at 30kV acceleration voltage.

Relative contents of copper, nickel, silica and alumina were determined using an energy dispersive micro-XRay Fluorescence spectrometer M4 TORNADO (Bruker) equipped with two anodes - a Rhodium X-ray tube of 50 kV/600 µA (30 W) and a Tungsten X-Ray tube of 50 kV/700 µA (35 W). For sample characterization, the Rhodium X-rays with a poly capillary lens that enables the excitation of 200 µm area was used. The detector employed was a Silicon-Drift-Detector Si (Li) with a Peltier cooling unit (253 K) and with a resolution of <145 eV at 100000 cps (Mn Kα). The measurements were performed under vacuum (20 mbar) using a few milligrams of dried powder samples placed in a multi-well plates, each of 2 mm thickness. For each sample, 25 points were measured in order to cover the sample surface with a spot size of 200 µm each. Quantitative analysis was done using fundamental parameter (FP) (standardless). Quantification of the weight percent of each element was done considering the stoichiometric formula of SiO_2 and Al_2O_3 for silica and alumina, respectively.

2.3. Catalytic hydrogenation of glucose

The catalytic tests were carried out on a SPR (Screening Pressure Reactor) multi reactor from Freeslate equipped with 24 reactors. In a standard test, 10 mg of catalyst were placed in each reactor and activated in H_2 at 300°C for 2 hours. Then, 3 mL of the aqueous glucose solution (1 wt.%) were injected into each reactor and the catalytic tests were performed at 130 °C and 30 bar hydrogen

pressure for 4 hours with a stirring at 800 RPM. The products obtained were analyzed using an HPLC Dionex equipped with a Rezex column and using UV and RI detectors. The conversion of glucose (X) was calculated as follow:

$X = 100 * [n(t_0) - n(t_f)] / n(t_0)$

where $n(t_0)$ and $n(t_f)$ are the number of moles of glucose at the t_0 and at the end of the reaction t_f, respectively.

The yield (Y) was calculated with the quantity of product obtained during the reaction. It is expressed as follows:

$Y = 100 * n_{prod}(t_f) / n_{reag}(t_0)$

where n_{prod} and n_{reag} are number of moles of product and of the substrate, respectively.

3. Results and discussion

3.1 Exploitation of the synthesis DoE

Firstly, the syntheses of 36 different catalysts have been conducted in the REALCAT high-throughput equipment using 36 possible variations in the preparation conditions obtained using a DoE, as aforementioned (see Table S1 in supporting information). Since the main aim of this study was to optimize the best conditions for the precipitation-reduction of metal on the support, the quantity of precipitated metal and "response variable" (obtained/expected) were determined using XRF for all catalysts. Further, the evaluation of the effect of individual factors in the DoE experiments, the influence of possible interactions between these factors and the precision in the evaluation were all determined by treating the values of "response variable" in the Minitab® software. The statistical analysis results for the evaluation of aforementioned effects and their interactions are further explained below in this section.

Table 3. P-values calculated for different factors used in DoE

Factors	P-value
Support	0.00
Precursor quantity	0.18
Precursor Type	0.18
Temperature	0.54
N_2H_4/H_2O molar ratio	0.03

The significance of the effect of each factor on the catalysts syntheses was determined using a parameter known as "P-value". This value represents the probability of the effect of a factor being solely due to random error. Thus, if the P-value for a factor is less than 5%, the effect of corresponding factor can be considered as significant. Table 3 shows the P-values calculated for the five factors used in the DoE. Hence, the type of support had the lowest P-value indicating that it was the most influential

parameter on the catalysts syntheses by precipitation followed by N_2H_4/H_2O molar ratio with a P-value of 0.03. The temperature had the highest P-value of 0.54 thus it was the least influential factor on the catalysts syntheses. During the analysis, a Pareto chart of the standardized effects could be used as it is a simple way to rank the effects and the significance of the factors and their interactions, in the order of their importance. Its objectives are: to reveal the essential factors of DoE experiments and their interactions - including the 3rd order interaction (interaction between 3 factors), to rank and to perform evaluation of their statistical significance. The effect of all factors, their interactions as well as the quadratic terms have been standardized (each effect divided by its standard error). The length of each bar in the diagram is proportional to the absolute value of its associated regression coefficient or its estimated effect. Additionally, the order of the bars displayed from top to bottom in the diagram corresponds to the order of significance of the effects of factors/interactions. Further, a statistical evaluation was done by calculating the significance threshold with a risk 'α' (α = 0.05). The chart also includes a vertical line (2.26 in Fig. 2) that corresponds to the 95% limit indicating statistical significance. An effect arising from the factors or their interaction will be therefore considered significant enough if its corresponding bar extends beyond this vertical line.

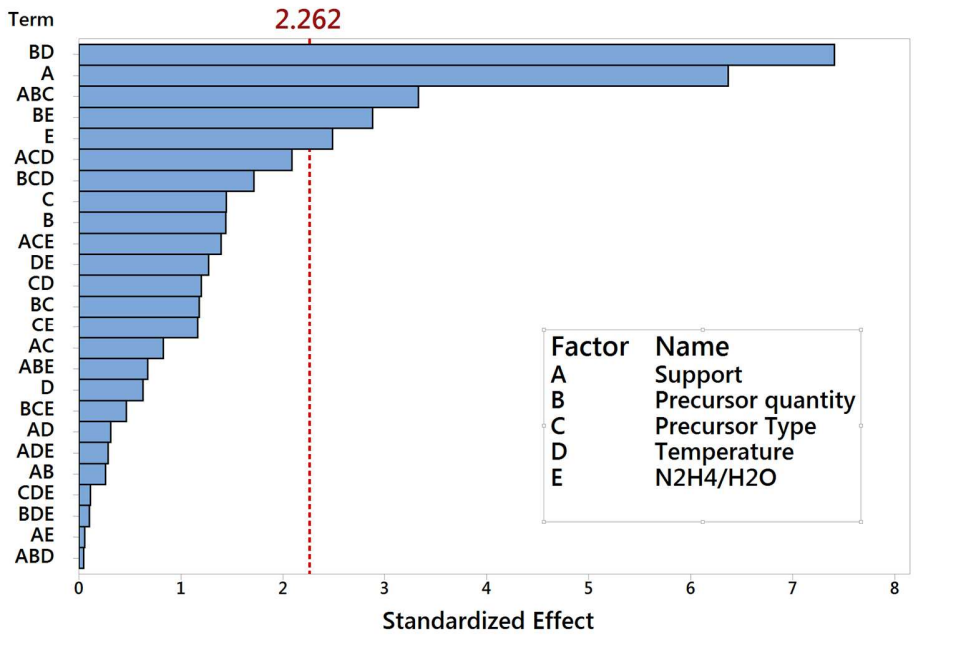


Figure 2. Pareto chart of the standardized effect of factors and their interactions in DoE experiments

The Pareto chart reveals that the effect of the interaction (BD) between precursor quantity and temperature followed by the support type (A) are the most significant effects on the precipitation of metals in DoE experiments. Furthermore, the interaction (ABC) between the support, precursor quantity and precursor type is the only observed significant effect of 3rd order interaction as clearly shown in the diagram (Figure 3). The effect resulting from the interaction (BE) between the precursor type and hydrazine/water molar ratio and from the factor hydrazine/water ratio (E) are also significant but less important, as these effects (BE & E) lie very close to the limit of significance (2.62).

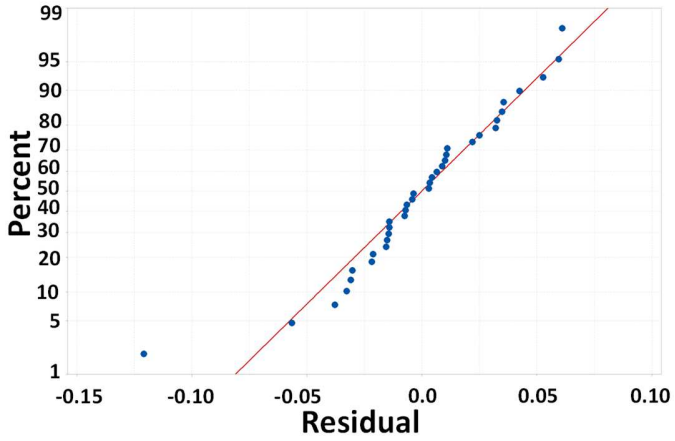


Figure 3. Normal probability plot of residuals in the model (Response = Obtained/Expected)

The "normal probability plot" permits to assure that all model assumptions have been met, hence describing the quality and accuracy of the model used (Figure 3). The plot of residuals (difference between observed and predicted value) shows that all residual points lie closer to the normal distribution line with only one point lying slightly far from it confirming that the used model meets the assumptions of normal distributions. Then, the model was used to determine the optimal set of synthesis conditions to get the best metal precipitation. From the above DoE analysis and the model used the optimum condition for the synthesis of a catalyst with better metal precipitation has been derived (Table 4).

Table 4. Optimum condition for the catalyst synthesis by precipitation

Parameters	Optimal
Support	Al_2O_3
Precursor quantity (wt.%)	5
Precursor type	Ni
Temperature (°C)	70
N_2H_4/H_2O (mol/mol)	0.04

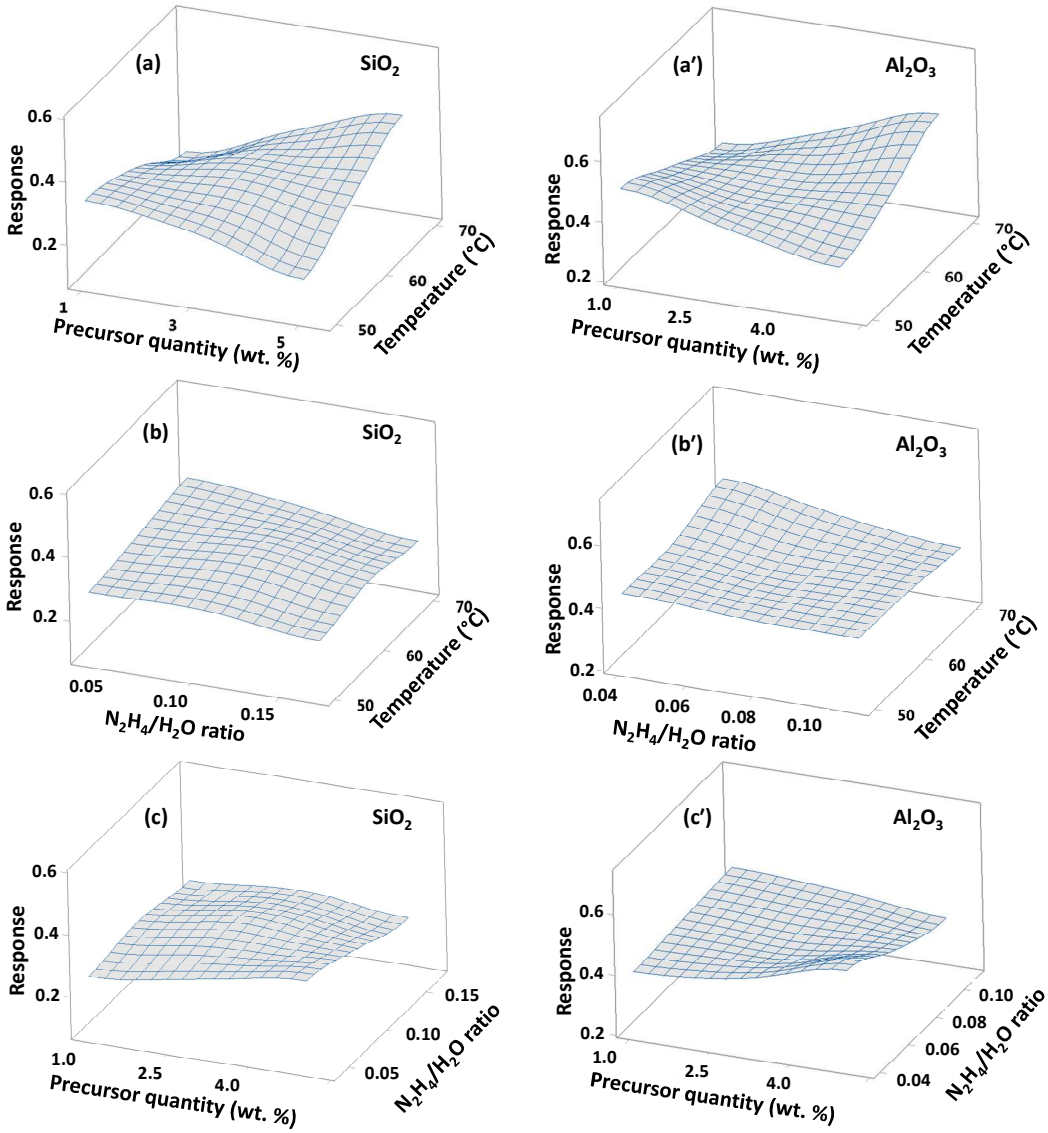


Figure 4. 3D surface plots depicting the relationship between response and two different predictor variables; Response *vs* (a) temperature & precursor quantity (b) temperature & N_2H_4/H_2O, (c) N_2H_4/H_2O & precursor quantity for SiO_2. Response *vs* (a') temperature & precursor quantity (b') temperature & N_2H_4/H_2O, (c') N_2H_4/H_2O & precursor quantity for Al_2O_3.

Finally, 3D surface plots have been plotted to clearly demonstrate the relationship between the response variable (obtained/expected) and any two conditions of synthesis (temperature, precursor quantity, N_2H_4/H_2O molar ratio) (Figures 4a-c & 4a'-c'). As the support was found to be a factor that exhibited significant effect, the experimental design studies were performed for both SiO_2 and Al_2O_3 supports. Therefore, a total of six surface plots, three each for SiO_2 and Al_2O_3, were plotted by changing the preparation conditions (predictor variables) around x- and y- axes but keeping the response (ratio of the quantity of effectively precipitated metal determined by the XRF analysis, to the theoretical quantity) always at z-axis (see Figure 4). Since response variable (obtained/expected) is an indirect representation of the % of the metal precipitated out of the total amount of metal used during synthesis, it is the

response variable used in z-axis of all the plots in Figure 4. Figures 4a and 4a' depicts the relation of the quantity of metal precipitation with the precursor quantity and temperature for SiO_2 and Al_2O_3 supports respectively. It is clear from both figures that the metal precipitation reached maximum at higher temperature and at higher amount of metal precursor used irrespective of the support. This is in good agreement with the model equation that showed a positive effect on metal precipitation using high levels of temperature and precursor quantities. It should be noted that if either one among the predictor variables (temperature or precursor quantity) was kept at lower level, it resulted in lower metal precipitation even if the second predictor variable was at higher level, hence once again confirming the significance of the interactions between the two factors. Figures 4b and 4b' show the metal precipitation as a function of the temperature and N_2H_4/H_2O ratio on SiO_2 and Al_2O_3 supports respectively. In both the supports, the maximum metal precipitation occurred at higher temperature and lower N_2H_4/H_2O ratio which is in good agreement with the model that exhibited a positive effect on metal precipitation for lower level of N_2H_4/H_2O ratio. This is in good agreement with the literature data [18-19, 23]. Higher hydrazine/water ratio can give rise to different Cu or Ni complexes. Hydrazine is a basic ligand and offers the possibility of different types of coordination when put in contact with transition metals such as Cu and Ni. It can form a monodentate ligand but at higher concentration may play the role of a chelating ligand. In this case the formation of stable complexes occurs and the reduction of metal is less probable. Another complication is due to the potent reducing properties of hydrazine in aqueous solutions. Depending on the nature of the metal ion involved several redox reactions can occur at the same time as the coordination process. Similarly, if predictor variables used are the precursor quantity and N_2H_4/H_2O ratio, then higher metal precipitation occurred at lower N_2H_4/H_2O ratio and at higher precursor quantity (Figures 4c and 4c'). As a partial conclusion, the synthesis of a set consisting of 36 catalysts were performed and the conditions required for the maximum precipitation of Ni and Cu metals were optimized in a short time period of around two days using the HT approach.

3.2. Characterization of catalysts

3.2.1. X-ray diffraction

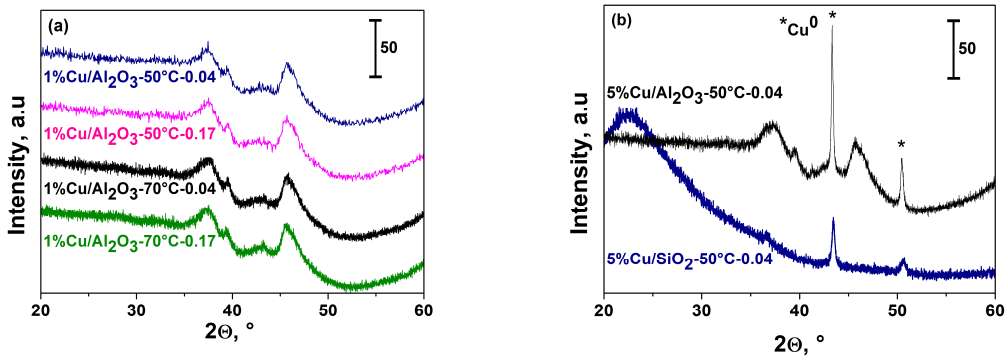


Figure 5. XRD patterns when (a) 1 wt.% of Cu precursor were used during syntheses under different conditions and (b) 5 wt.% of Cu precursor were used during syntheses at 50 °C and N_2H_4/H_2O molar ratio of 0.04

Figure 5a shows the X-ray diffractograms of 1 wt.% Cu/Al_2O_3 catalysts synthesized at different conditions. In the diffraction pattern of 5 wt.% copper on silica (Figure 5b), a Cu in cubic structure (2Θ = 34.7º - PDF_01-077-8628) was observed. As expected, no peaks of metallic copper were observed for the catalysts with 1 wt.% Cu, whatever the temperature of the synthesis (50 or 70 °C) and N_2H_4/H_2O molar ratios (0.04 or 0.17). Similarly, the diffraction peaks from metals were not observed irrespective of the supports (SiO_2 or Al_2O_3) and metal precursors (Cu or Ni) when 1 wt.% of metal was used during the synthesis (data not shown here). This confirms that the amount of metal deposited on the support was too low to be detected by XRD. It is in good agreement with XRF results that showed only ~0.2 wt.% to ~0.5 wt.% of metal amount on catalysts synthesized using 1 wt.% of metal precursor. On the other hand, for all the catalysts prepared with 5 wt.% of metal precursors, the corresponding metal peaks appeared in the diffractograms of all catalysts irrespective of other conditions. For example, two sharp peaks of metallic Cu^0 were observed at 2θ = 43.2° and 50.4° for the 5 wt.% Cu supported on both Al_2O_3 and SiO_2 (Figure 5b).

3.2.2. Scanning electron microscopy (SEM)

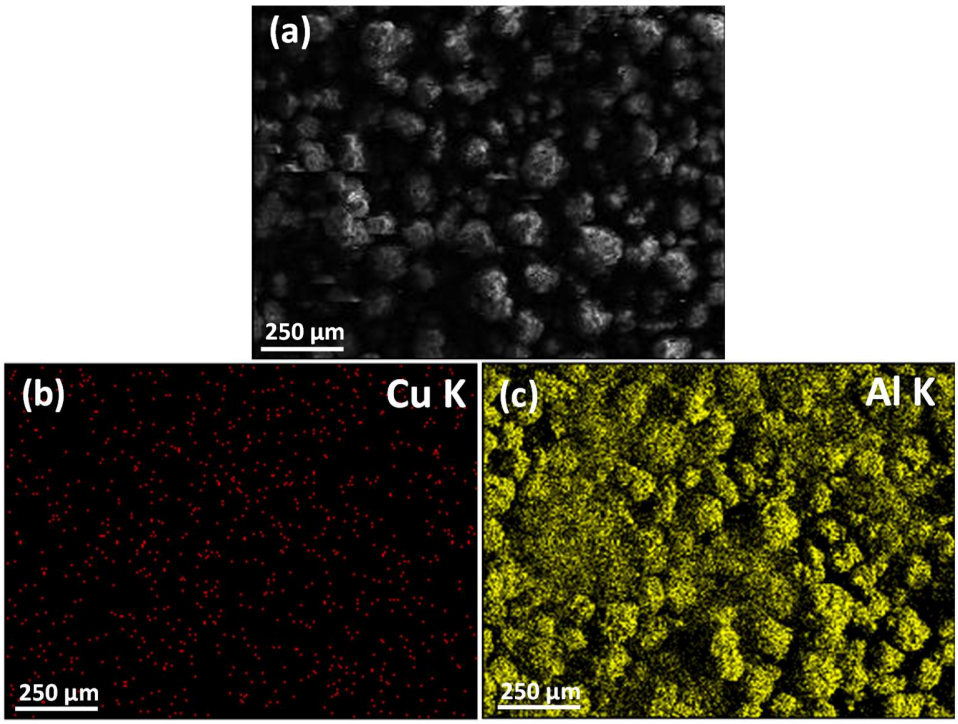


Figure 6. Example of SEM image (a) and EDX analyses for 1 wt.% Cu/Al_2O_3 catalyst (b and c)

In order to verify the homogeneity in the distribution of the metal particles on support, SEM and EDX analysis were performed for Cu/Al_2O_3 and Cu/SiO_2 catalysts. Figure 6a shows that in 5wt.% Cu supported on Al_2O_3 catalyst, the support particles are irregular shaped spheres with the particle size ranging from ~100 to 200 µm. The surface mapping of the catalyst indicates the homogenous distribution of metallic Cu on Al_2O_3 support (Figures 6b and 6c). The tiny red dot in the nano-scale range enables an indication of metallic Cu distribution (Figure 6b). In case of Cu supported on SiO_2, similar homogeneous distributions of metallic Cu nano particles were observed (see Figure S1 in supporting information). Hence, SEM

analysis confirms that the HT syntheses by precipitation reduction method equally resulted in catalysts with homogeneously distributed metal nano-particles, as given by a traditional catalyst synthesis procedure.

3.3. High-throughput glucose hydrogenation tests

The activities of all synthesized catalysts were further screened for glucose hydrogenation reaction in a high-throughput SPR equipment containing 24 batch reactors. Glucose conversions obtained at 130 °C for the catalysts prepared at different temperatures (50 and 70 °C) using alumina or silica as supports are shown respectively in Figures 8a and 8b.

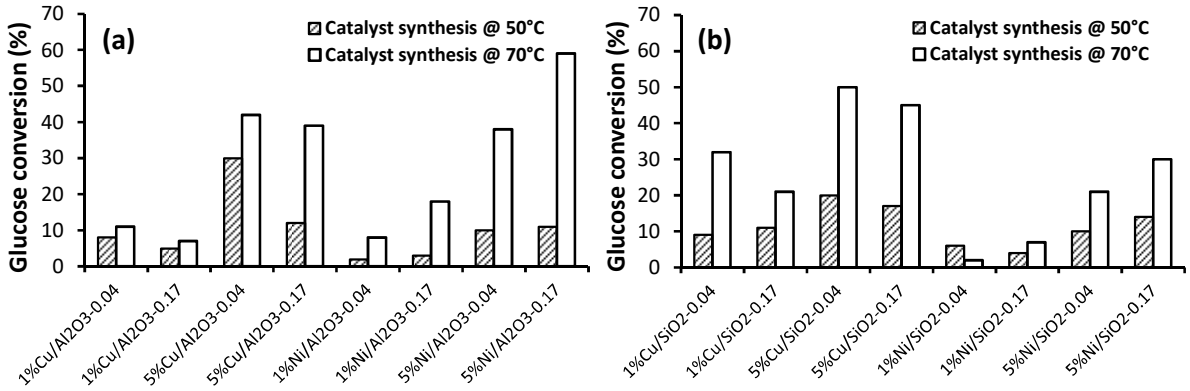


Figure 8. Glucose conversions with (a) Alumina-supported and (b) Silica-supported catalysts synthesized at temperatures 50 and 70 °C. (Test conditions: Catalyst amount=10 mg, 3 mL of glucose solution (1 wt.%), T=130 °C, P_{H2} = 30 bar, t = 4h)

The test results using central (zero) level catalysts are not included in this study, since the catalysts were prepared at entirely different conditions than that of catalysts at high and low levels. Figures 8a and 8b clearly show that the glucose conversion is higher for all the catalysts (except 1%Ni/SiO_2-0.04) synthesized at 70 °C compared to their corresponding counterparts synthesized at 50 °C, irrespective of the metal precursors, supports and hydrazine/water ratios employed during catalysts syntheses. It could be supposed that higher temperature of reduction permits better metal reduction. It was already observed in the literature that the increase of the temperature permits a better and faster decomposition of the intermediate complex formed between the metal salt and hydrazine [18-19, 23]. This would increase the overall reduction extent thereby influencing the catalytic activity. Similarly, the yield to the major product sorbitol is higher for the catalysts synthesized at 70 °C (Figures 9a and 9b). Hence, only the test results with catalysts synthesized at 70 °C will be considered further for comparison of the test results.

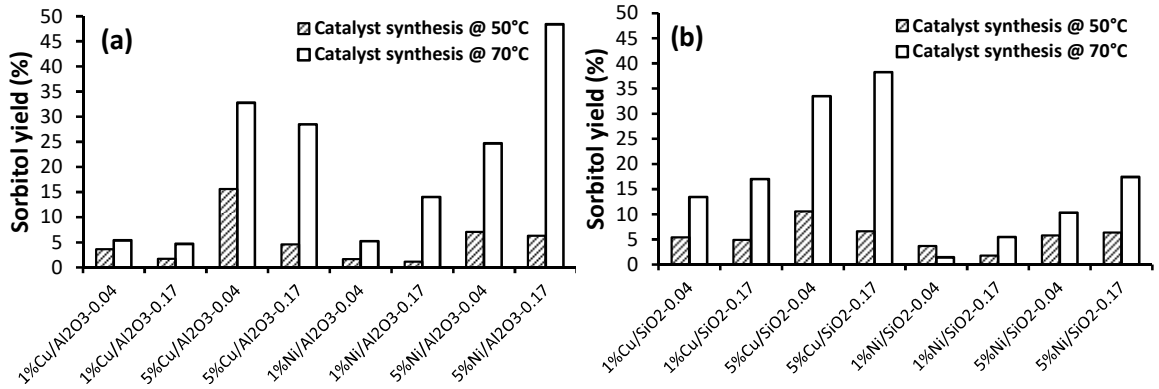


Figure 9. Sorbitol yields with (a) Alumina-supported and (b) Silica-supported catalysts synthesized at temperatures 50 and 70 °C. (Test conditions: Catalyst amount=10 mg, 3 mL of glucose solution (1 wt.%), T=130 °C, P_{H2} = 30 bar, t = 4h)

The catalysts prepared using different hydrazine/water ratios differ in their catalytic activity towards sorbitol yields at 70 °C (Figure 10). In the alumina-supported catalysts (Figure 10a), when the Cu was used as the metal, the sorbitol yields are higher for the catalysts with lower hydrazine/water molar ratio (0.04) than for catalysts prepared with higher ratio (0.17). The trend was reversed, i.e. the higher sorbitol yields for the catalysts with higher hydrazine/water ratio (0.17), when Ni was used instead of Cu (Figure 10a). Unlike alumina-supported catalysts, the silica supported catalysts prepared at higher hydrazine/water ratios (0.17) consistently exhibited higher sorbitol yields compared to their counterparts prepared at lower hydrazine/water ratios (0.04) (Figure 10b).

The catalysts with higher hydrazine/water ratios showed maximum sorbitol yields in most cases, except for 1 wt.%Cu/Al_2O_3 and 5 wt.%Cu/Al_2O_3 catalysts that showed slightly lower or relatively similar activities at lower hydrazine/water ratios. Thus, we could conclude that the catalysts prepared at higher hydrazine/water ratio can exhibit more activity to give sorbitol. It is also clear from Figure 10 that the catalysts with 5wt% metal loading showed higher sorbitol yields compared to that with 1 wt.% loading, irrespective of the supports and metal precursors used. Hence, all the aforementioned results confirmed that the catalysts prepared at higher temperature (70 °C), hydrazine/water ratio (0.17) and quantity of metal precursor (5 wt.%) rather yielded maximum amount of sorbitol than their lower level counterparts (50 °C, 0.04, 1 wt.%) under the conditions employed in this study. This could be explained by the reduction mechanism of metal ions by hydrazine in aqueous medium. Indeed, the extent of the reduction of metal salt strongly depends on the kinetic of decomposition of the complex formed between metal salt and the hydrazine ions [23]. It was observed that in the case of nickel reduction at low temperature, the decomposition of the complex could take much more time (hours) than for the Cu ions (minutes) [23]. The complete decomposition of the complex and the reduction of nickel could be accelerated by increase of reduction temperature.

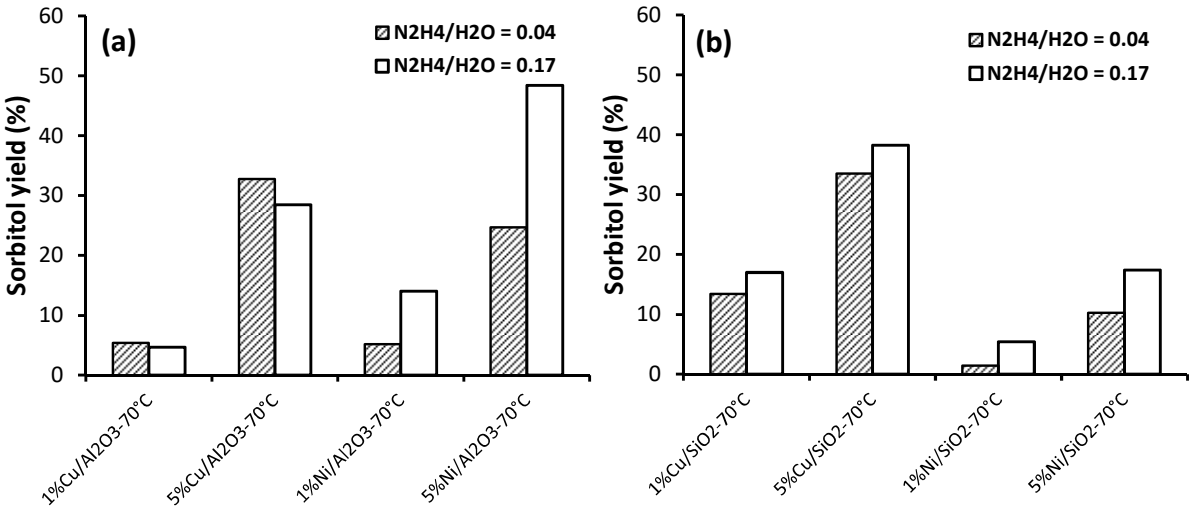


Figure 10. Sorbitol yields with (a) Alumina-supported and (b) Silica-supported catalysts synthesized at two different hydrazine/water ratio at 70 °C (Test conditions: Catalyst amount=10 mg, 3 mL of glucose solution (1wt.%), T=130 °C, P_{H2} = 30 bar, t = 4h)

Finally, the sorbitol yields obtained using the catalysts synthesized at "high-level" conditions (namely 70 °C, 0.17, 5 wt.%) were compared (Figure 11). The SiO_2-supported catalysts showed higher sorbitol yield when the metal used was Cu (38.3%) compared to its Ni counterpart (17.4%). In contrast, higher sorbitol yield is obtained using Al_2O_3-supported catalysts with Ni (48.4%) compared to that with Cu (28.5%). In short, among all the catalysts synthesized, 5%Ni/Al_2O_3-70°C-0.17 is the catalyst that showed highest sorbitol yield (48.4%) followed by 5%Cu/SiO_2-70°C-0.17 (38.3%) under the conditions employed in this study. The relatively high sorbitol yield obtained with the 5%Cu/SiO_2 catalyst is of interest as compared with the 5%Ni/SiO_2 catalyst. The use of nickel should be somehow restricted because of the toxicity of the Ni^{2+}. Therefore, we show here that Cu based catalysts could replace nickel for the selective hydrogenation reaction.

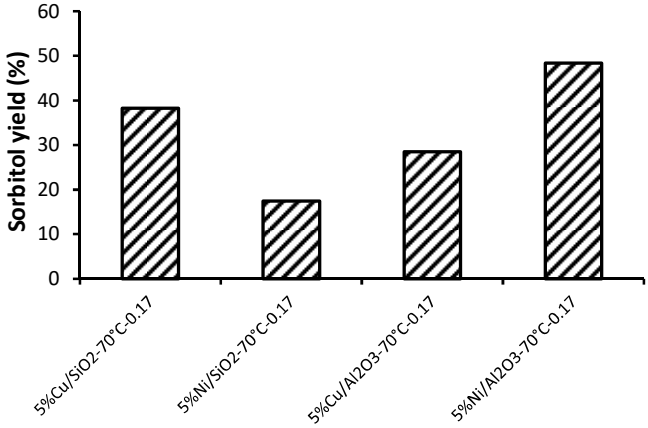


Figure 11. Sorbitol yield on 5 wt.% metal loaded catalysts synthesized at 70 °C and hydrazine/water molar ratio = 0.17. (Test conditions: Catalyst amount=10 mg, 3 mL of glucose solution (1wt.%), T=130 °C, P_{H2} = 30 bar, t = 4h)

It is interesting also to note that there is no direct correlation between the nature of the support and the metal. As could be seen from Figure 11, the highest yield was observed for Cu supported on silica and Ni supported on alumina. This could be also directly linked to the mechanism of the reduction of both metals by hydrazine. Indeed, the reduction of metal ions (by hydrazine) strongly depends on the nature of the support. The driving force of the chemical reduction by hydrazine in aqueous media is the difference between the redox potentials of the two half-cell reactions, ΔE [24]. As it could be expected the reduction of the metal is thermodynamically possible only if ΔE is higher than 0. This implies that the redox potential of the reducing agent (such as alcohols, polyols, hydrazine) must have a more negative value than the corresponding metal ion [24]. Moreover, the ΔE should be larger than 0.4 V. If the ΔE is lower the reaction may not proceed or proceed very slowly to be of any practical importance [24]. Taking this into account, strongly electropositive metals like Au, Pt, Pd, Cu will react easily under mild conditions and with a large number of reducing agents. Contrary to that the more electronegative metals like Ni, or Co will require stronger reducing agents and, frequently, harsher conditions (temperature, pressure or longer time) [24]. Moreover, the chemical reduction of more electronegative metals with hydrazine strongly depends also on the extent of the interaction between hydrazine and the support. In this case the reduction of the metal is slow and the hydrazine can interact with the support (acid sites of the support). As reported in the literature, reducible supports permit faster reduction of nickel [23]. Contrary to that strongly acid supports stabilized the nickel ion/hydrazine complex making the reduction slower and sometimes it can completely stop it [19].

It is also remarkable to note that the glucose hydrogenation tests reported here have been performed with all 36 catalysts in a time span of just two days using the HT approach, therefore saving enormous time and energy.

4. Conclusions

A high-throughput approach has been used to not only synthetize and characterize Ni- and Cu- based catalysts supported on SiO_2 and Al_2O_3 but also for catalytic screening in liquid phase glucose hydrogenation to sorbitol. We successfully demonstrated that a design of experiments approach (DoE) and HT methods enabled the synthesis of a set of 36 catalysts and optimization of the suitable conditions required for the maximum precipitation of Ni and Cu metals using a reduction-precipitation method. Irrespective of the supports used in this study, the maximum metal precipitation occurred at higher temperature and lower N_2H_4/H_2O molar ratio which is in good agreement with the proposed model. Similarly, the higher metal precipitation occurred at lower N_2H_4/H_2O ratio and at higher precursor quantity in agreement with the DoE model that was employed to determine theoretically the most favorable conditions for the deposition of metals by the reduction-precipitation method. XRD confirmed the presence of metallic Cu and Ni when 5 wt.% precursor was used during synthesis but these metals were not observed for catalysts synthesized using 1 wt.% of metal. SEM-EDX confirmed the homogeneous deposition of the metals on the supports using the reduction-precipitation method indicating that the robotized preparation of the catalysts gives similar results as the manual protocol. Furthermore, glucose hydrogenation tests have been performed with all 36 catalysts over a short period of just two days using the HT approach. The sorbitol yields were higher for the catalysts synthesized at

high-level conditions (70 °C, 0.17, 5 wt.% of metal) compared to the catalysts synthesized at low-level conditions (50 °C, 0.04, 1 wt.% of metal) irrespective of the support and metal precursor used. The Cu/SiO_2 catalysts exhibited higher activity in glucose hydrogenation compared to Ni/SiO_2 whereas, Ni/Al_2O_3 showed higher activity compared to Cu/ Al_2O_3.

Hence, in this work we succeeded to synthesize, characterize and screen the whole library of catalysts for glucose hydrogenation reaction within a total time span of around 5 days using the HT approach. This permitted to save a lot of time and energy compared to the conventional laboratory processes, which would have taken at least 6 times more days (~30 days) of work to get the same results. HT methods can thus reduce the time and energy constrains to move new biomass catalysis processes from the laboratory to the industrial scale and thus have a great scope in this fast moving world of catalysis.

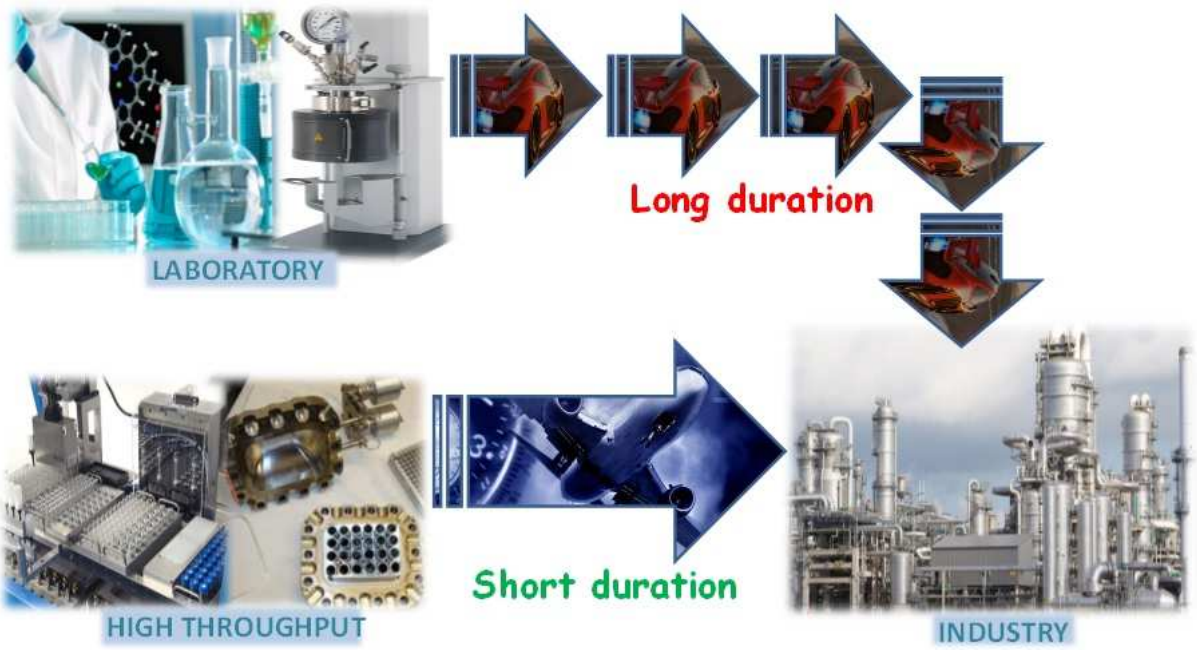
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High-throughput (HT) methodology was applied for the synthesis, characterization and catalytic testing of Cu- and Ni-based catalysts for glucose hydrogenation. Design of Experiment (DoE) was used in all steps. The deposition and reduction of both metals was performed using chemical reduction with hydrazine method. In total 36 catalysts were synthetized, characterized and tested in 5 days. The amount of metal deposited on the support was chosen as the discriminative and determining parameter. The catalysts were tested at low temperature in the hydrogenation of glucose to sorbitol.