

# Hydrogen production by aqueous phase reforming of sorbitol using bimetallic Ni–Pt catalysts: metal support interaction

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**Abstract** Hydrogen was produced by Aqueous Phase Reforming (APR) of 10% (w/w) sorbitol using mono- and bi-metallic catalysts of Ni and Pt supported on alumina nano-fibre (Alnf), mesoporous ZrO<sub>2</sub> and mixed oxides of ceria–zirconia–silica (CZxS) with varying concentration of silica (where *x* is silica concentration). X-ray diffraction, TEM/EDS and temperature programmed reduction were also carried on these catalysts to study the surface properties. It was observed that co-impregnation of Pt and Ni in atomic ratio 1:12 increased the reducibility of Ni by forming an alloy. However, sequential impregnation of Ni followed by Pt does not form the bi-metallic particles to increase the Ni reducibility. Reduction peak of co-impregnated Ni–Pt/Alnf was found to be 270 °C lower than the sequentially impregnated Pt/Ni/Alnf. The presence of silica at high concentration in CZxS support decreased the reducibility of ceria by forming an amorphous layer on Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> crystals, which also decreased Ni reducibility. The rate of H<sub>2</sub> formation from aqueous phase sorbitol reforming was found to be highest for co-impregnated Ni–Pt catalysts followed by sequentially impregnated Pt/Ni and monometallic Ni catalyst. The H<sub>2</sub> activity decreased in the following order of the supports: Alnf > ZrO<sub>2</sub> > CZ3S > CZ7S.

**Keywords** Bimetallic Ni–Pt catalyst · Aqueous phase sorbitol reforming · TPR

## Introduction

Conversion of biomass to fuels has been a subject of research for many years because of its environmental benefits and renewability. Aqueous phase reforming of oxygenated hydrocarbons, like alcohols and polyols, to produce hydrogen, has been especially of great interest [1–6]. In our previous studies, we have reported hydrogen production from ethylene glycol, sugars and sorbitol using noble metals supported on high surface area mesoporous supports [4–6]. In particular, our recent report showed that addition of minute quantities of noble metals to Ni, forms alloy catalyst which increased the rate of hydrogen formation from aqueous phase reforming of sorbitol by 3–5 times [7]. The increase in the activity was believed to be due to two factors—first, the increase in reducibility of the Ni catalysts resulted in higher number of active sites. Second, the alloying of Pt and Ni decreased the CO binding energy on the active metal site which reduced catalyst poisoning and also increased the fraction of active sites available for the reforming reaction. It was suggested in the report that co-impregnation of Pt and Ni may prevent the formation of nickel aluminate, which is formed during calcination at temperature in excess of 450 °C [7, 8]. This enables reduction of the catalysts at lower temperature resulting in higher dispersion [7]. However, Shu et al. [9] reported that at low Ni concentration, the impregnation sequence has a significant impact on the Ni–Pt catalyst supported on alumina. The alloying of Ni–Pt was found to occur at 1:1 concentration regardless of the impregnation sequence. The alloy catalyst was also reported to be higher

This manuscript is dedicated to Prof. Jack Harrowfield and Dr. Jacques Vicens on the celebration of their 65th birthday.

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in activity compared to monometallic and non-alloy bimetallic catalysts. Alloy catalysts, especially with noble metals as promoters, have been subject of interest for various applications because of their enhanced activity [10–16]. Therefore, it is desirable to select supports and preparation methods which can achieve alloying of noble metals with non-precious metal like Ni. This is also important for reducing the cost of the catalyst. In this report, we study the effect of impregnation sequence of Ni and Pt supported on alumina nano-fibre (Alnf), mesoporous zirconia ( $\text{ZrO}_2$ ) and mixed oxide of ceria–zirconia–silica (CZxS) with 5% ceria and varying concentration ( $x = 3, 7, 9$  and 11%) of silica. Alnf,  $\text{ZrO}_2$  and CZxS supports were prepared to study the effect of support on the reducibility and activity of the catalyst for aqueous phase reforming of sorbitol solution in water. Ceria and zirconia based mixed oxide supports have been extensively researched in the recent past for variety of reactions such as low temperature water gas shift [17], preferential CO oxidation [18, 19] and methanol reforming [20]. The mixed oxides performed better than the individual oxides due to their higher hydrothermal stability and oxygen storage capacity which is desirable in preferential oxidation of CO [19, 21]. Transition metal catalysts supported on the mixed oxide supports may vary in their reducibility and activity depending upon the type of support used [22, 23]. This is believed to be due to the difference in metal support interaction leading to variation in metal crystallite size and dispersion [22]. In this study, we analyse the effect of this interaction on the bimetallic Ni–Pt catalyst using XRD, TEM/EDS and temperature programmed reduction. A fixed bed reactor was used to test the activity of these catalysts for the aqueous phase reforming of sorbitol solution to produce  $\text{H}_2$ .

## Experiments and methods

### Catalyst preparation

To prepare ceria–zirconia–silica support desired amount of  $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  (Aldrich) was dissolved in 750 mL water and desired amount of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Aldrich) was added. Fine powder  $\text{SiO}_2$  was dispersed in 1,000 mL  $\text{H}_2\text{O}$  until clear solution was achieved. The zirconium nitrate and cerium nitrate solution was added drop-wise to the  $\text{SiO}_2$  solution along with 2.5 mol/L NaOH in 250 mL water until  $\text{pH} = 10$  was reached. The resulting precipitates were vigorously stirred for 24 h. The solids were centrifuged and washed many times with deionised water. The solids were dried at 110 °C and calcined at 550 °C for 6 h. The preparation methods for alumina nano-fibre (Alnf) and  $\text{ZrO}_2$  are given elsewhere [6, 7]. Desired amount of

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Aldrich) and 8%  $\text{H}_2\text{PtCl}_6$  solution in water (Aldrich) was used to impregnate Ni and Pt, respectively. For sequential impregnation (Pt/Ni), Ni was impregnated first by adding desired amount of precursor along with water. The solution was stirred constantly at 60 °C for 5 h followed by calcination at 650 °C (CZxS) and 500 °C ( $\text{ZrO}_2$  and Alnf) for 6 h. Pt was impregnated on the calcined Ni catalysts by wet impregnation method at 60 °C with constant stirring for 5 h followed by calcination at 500 °C. For co-impregnation (Ni–Pt) the Ni and Pt precursors were added simultaneously along with water and stirred constantly at 60 °C for 5 h and the resulting catalysts were air dried and calcined at 500 °C.

### Catalyst characterisation

The supports were characterised by  $\text{N}_2$  adsorption technique in Quantachrome Autosorb 1C instrument to measure the BET surface area. The metal loading of the catalysts were determined by Varian Vista Pro ICPAES instrument from an external source. X-ray Diffraction (XRD) was carried out using Rigaku Miniflex diffractometer employing  $\text{Co K}\alpha$  radiation source. Temperature programmed reduction (TPR) was carried out using 5%  $\text{H}_2/\text{N}_2$  mixed gas flow at 50 mL/min. Aqueous phase reforming of sorbitol was carried out in a fixed bed reactor. The complete TPR and fixed bed reactor setups and the experimental procedures are given in our previous report [7].

## Results and discussion

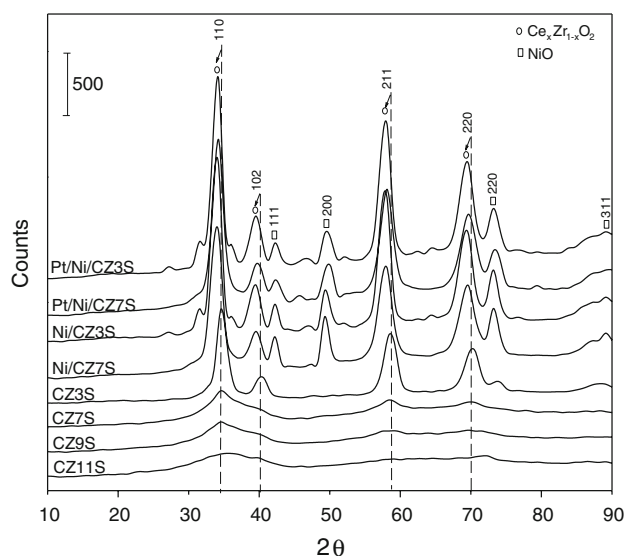
Table 1 shows the metal loading and the BET surface area of the catalysts used in this study. All the metal loading values mentioned in Table 1 are the measured values determined by the ICP analysis. CZ9S and CZ11S with 9 and 11% silica, respectively, were not selected for the study of the effects of impregnation sequence because of their similarity with the CZ7S supports (Figs. 1 and 2). Therefore, the metal loading values of the bimetallic catalysts are shown only for Alnf,  $\text{ZrO}_2$ , CZ3S and CZ7S. All the metal loadings are approximately in the range of 7% Ni and 2% Pt, making the atomic ratio of Pt:Ni approximately 1:12.

### XRD results

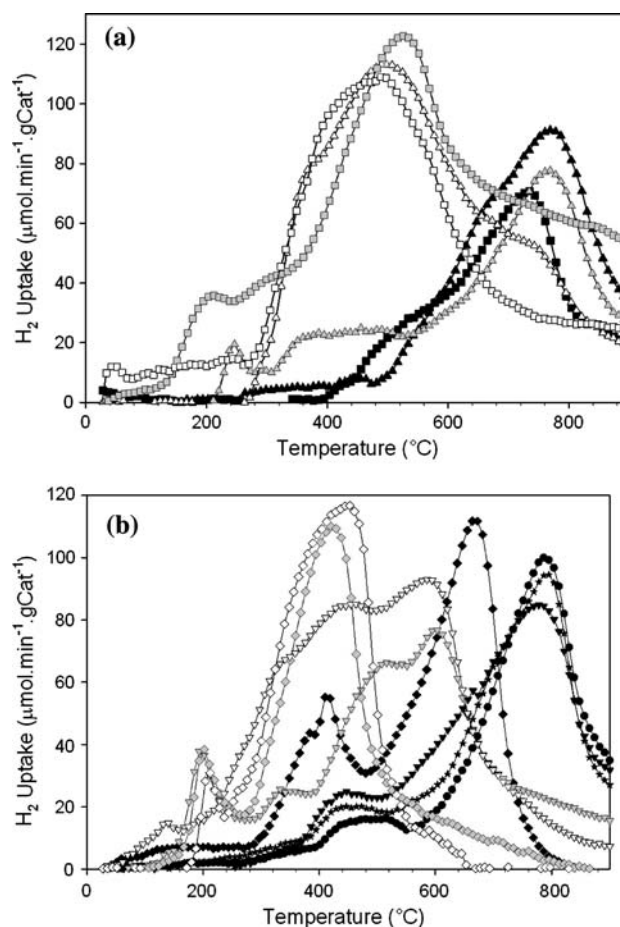
Figure 1 shows the X-ray diffractograms of the CZxS support series and the selected catalysts after impregnation. Figure 1 shows the 110, 102, 211 and 220 peaks of mixed oxide of ceria–zirconia of the form  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ . The XRD patterns did not show any features that suggest a presence of  $\text{SiO}_2$  in the lattice of ceria or zirconia. It is

**Table 1** Catalyst properties determined by the ICP and N<sub>2</sub> physisorption analysis

Support	Metal loading (% w/w)					BET surface area (m <sup>2</sup> /gm)
	Ni	Co-impregnated (Ni–Pt)		Sequentially impregnated (Pt/Ni)		
		Ni	Pt	Ni	Pt	
Alnf	6.71	6.50	0.96	6.92	2.08	360.47
ZrO <sub>2</sub>	7.01	7.18	1.86	7.06	1.99	240.90
CZ3S	6.78	7.89	1.60	6.31	1.74	110.09
CZ7S	6.53	7.63	1.68	6.71	1.78	220.10
CZ9S	6.74	–	–	–	–	261.09
CZ11S	6.73	–	–	–	–	306.43

**Fig. 1** XRD profiles of CZ<sub>x</sub>S support series, Ni and Pt/Ni catalysts supported on CZ3S and CZ7S. The broken lines mark the peaks for calcined CZ<sub>x</sub>S support which corresponds to the Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> crystallite form. The arrows point to the shifted Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> peak after impregnation of Ni (0)

known from previous literature that SiO<sub>2</sub> does not form any compound with ceria and zirconia [24, 25]. It is expected that SiO<sub>2</sub> is well dispersed on the ceria–zirconia solid solution. After impregnation of Ni the peaks of Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> shifts towards lower diffraction angle by approximately 1° 2θ. This may be due to the change in lattice parameter of Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> solid solution by the introduction of Ni. The Ni/CZ7S peaks are more crystalline compared to CZ7S because at the higher calcination temperature it is expected that ceria–zirconia solid solution is slightly sintered [25]. The NiO peaks shown in Fig. 1 correspond to the cubic phase. Impregnation of Pt does not change the lattice parameter and we did not observe a Pt peak in the XRD results. This is because Pt is present in very small quantity and it is expected to be highly dispersed. Figure 1 also shows that the addition of silica in higher concentration increases the amorphousness

**Fig. 2** TPR profiles of monometallic Ni (black), co-impregnated Ni–Pt (white) and sequentially impregnated Pt/Ni (grey) catalysts supported on (a) Alnf (up triangle) and ZrO<sub>2</sub> (square) and (b) CZ3S (diamond), CZ7S (down triangle), CZ9S (circle), and CZ11S (star)

of the support, which is validated by the increase in BET surface area observed in Table 1. In a study by Schulz et al. [26], a change in morphology of Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> crystals was observed with increasing amount of silica in a CZ<sub>x</sub>S material. It was noted that at 20% silica content an amorphous layer was found on top of spherical

crystalline  $Ce_xZr_{1-x}O_2$  core particles. This suggests that the silica concentration has a significant impact on the morphology which can affect the reducibility of the supported metals because of change in crystallite size.

#### Temperature programmed reduction

Figure 2a, b shows the results from temperature programmed reduction performed on the catalysts. The rate of hydrogen uptake, expressed as  $\mu\text{mol min}^{-1} \text{gCat}^{-1}$ , was measured with respect to the temperature. The peak of hydrogen uptake for Ni/Alnf is observed at 770 °C. The high temperature reduction peak is expected because of the strong interaction between Ni and Alnf at calcination temperature in excess of 450 °C [8]. The reduction peak of Ni/ZrO<sub>2</sub> is at slightly lower temperature (730 °C) and it also has lower on-set temperature. This is believed to be due to the reverse hydrogen spillover [22]. Pt/Ni/Alnf exhibits peaks at three different temperature ranges. The low temperature peak at 240 °C is most likely to be the Pt reduction peak. There is a broad region of reduction peaks from 300 to 550 °C which is expected to be reduction of NiO catalysed by the presence of Pt in the vicinity [7]. However, the major reduction peak is observed at 770 °C which is similar to Ni/Alnf. Therefore, it can be said that the Pt particles on Pt/Ni/Alnf are most likely to be segregated away from Ni particles because they are not able to catalyse the reduction of Ni [27]. The reduction peak of co-impregnated Ni-Pt/Alnf is shifted to 500 °C, which is 270 °C lower than the major reduction peak of Pt/Ni/Alnf and Ni/Alnf, strongly suggesting formation of a Ni-Pt bi-metallic particle. In case of ZrO<sub>2</sub> supported catalysts, we did not observe significant difference in the reducibility of the bi-metallic catalysts with different impregnation sequence. It can be noted, however, that Pt/Ni/ZrO<sub>2</sub> exhibited a shoulder peak at 200 °C and the major peak is slightly broader compared to Ni-Pt/ZrO<sub>2</sub> which may suggest that some Pt particles may not participate in the bi-metallic interaction due to greater distance from the Ni particles.

Figure 2b shows the effect of silica content in the mixed oxides support. Ni supported on CZ7S, CZ9S and CZ11S resulted in similar reducibility. These three catalysts exhibit a major peak at 790 °C and a broad minor peak at 450–500 °C. The broad low temperature peak is expected to be due to partial reduction of surface ceria [28, 29]. Ceria reduction peak is more prominent in Ni/CZ3S which is seen as a shoulder peak at 380 °C, however, with increasing concentration of silica it is expected that the amorphous silica layer on top of the  $Ce_xZr_{1-x}O_2$  crystals decreases ceria reducibility. The peak at 410 °C for Ni/CZ3S is likely to be NiO reduction peak, where NiO particles are not in strong interaction with the oxide

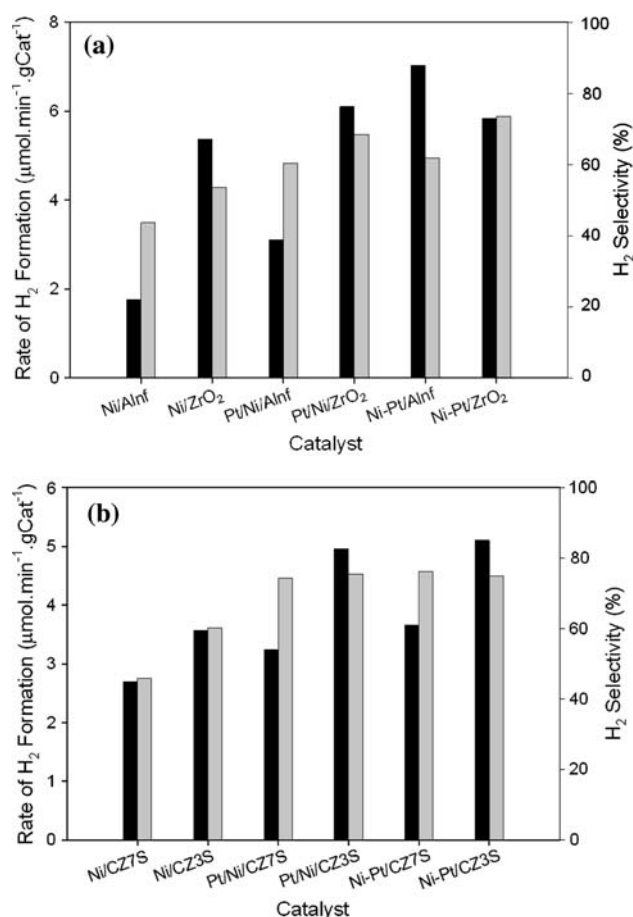
support [30, 31]. We also notice a peak at 660 °C which is similar to the peak observed at 790 °C for CZ7S–CZ11S supports. In this case, the peak is shifted towards the lower temperature because of the hydrogen spillover from the Ni particles reduced at 420 °C. With increasing concentration of silica, the  $Ce_xZr_{1-x}O_2$  crystallites may be covered with amorphous layer and the NiO particles are therefore stabilised, leading to increase in reduction temperature.

The bimetallic catalysts prepared on CZ7S and CZ3S did not display significant difference in reducibility with respect to the different impregnation sequences. The peaks for Ni–Pt/CZ3S (white diamond) and Pt/Ni/CZ3S (grey diamond) are almost identical. However, the sequentially impregnated catalysts (Pt/Ni/CZ7S and Pt/Ni/CZ3S) displayed a Pt reduction peak at 195 °C which is similar to the sequentially impregnated catalysts supported on ZrO<sub>2</sub> (Fig. 2a). This indicates that although there is some interaction between Pt and Ni particles there may be some Pt particles which are segregated away from Ni particles. The co-impregnated catalysts on the contrary display modification to the low temperature reduction peak. In case of Ni–Pt/CZ7S, the peak is broadened and while the Ni–Pt/CZ3S peak is shifted to slightly higher temperature, suggesting that the peak may correspond to bi-metallic particles reduction [7].

#### Aqueous phase reforming of sorbitol

Figure 3a, b shows the rate of H<sub>2</sub> production and the gas phase H<sub>2</sub> selectivity for the catalysts tested for reducibility. The results for Alnf supported catalysts are consistent with the results we have previously reported [7] for the co-impregnated catalyst. Sequentially impregnated Pt/Ni/Alnf is more active and selective than the Ni/Alnf, however, it does not match the performance of Ni–Pt/Alnf. The two possible reasons for this is that Pt/Ni/Alnf is less reduced compared to Ni–Pt/Alnf (despite similar metal loading and reduction procedure) and since Ni–Pt bi-metallic particle is not formed in Pt/Ni/Alnf, the resistance to strong CO binding is considerably lower than Ni–Pt/Alnf [7]. Therefore, we believe that strong metal-support interaction of Ni–Alnf in sequential impregnation inhibits the alloy formation [9] and reduces the catalytic activity of bimetallic catalysts. Also, co-impregnation of Ni–Pt can limit the Ni–Alnf interaction by forming an alloy, which has shown to be 3–5 times more active than Ni/Alnf for H<sub>2</sub> production from liquid phase reforming of sorbitol [7]. ZrO<sub>2</sub> supported bimetallic catalysts showed no effect of the impregnation sequence on the H<sub>2</sub> activity and selectivity, which was expected from the TPR results.

Figure 3b shows the results from CZxS supported catalysts and it can be observed that the bimetallic



**Fig. 3** Rate of H<sub>2</sub> formation (black) and gas phase H<sub>2</sub> selectivity (grey) from Ni and bimetallic catalysts supported on (a) Alnf and ZrO<sub>2</sub> and (b) CZ7S and CZ3S. H<sub>2</sub> selectivity is defined as  $[(\text{Ratio of H}_2/\text{C in gas phase})/RR] \times 100$ , where *RR* is the theoretical reforming ratio for 100% conversion of sorbitol to H<sub>2</sub> and CO<sub>2</sub> according to equation  $\text{C}_6\text{O}_6\text{H}_{14}(l) + 6\text{H}_2\text{O}(l) \leftrightarrow 13\text{H}_2(g) + 6\text{CO}_2(g)$

catalysts showed higher H<sub>2</sub> activity and selectivity compared to Ni catalysts. The rate of H<sub>2</sub> formation was significantly higher for CZ3S supported bimetallic catalysts compared to CZ7S. However, we did not observe similar difference in the H<sub>2</sub> selectivity. All the CZ<sub>x</sub>S supported bimetallic catalysts were approximately 75% selective for H<sub>2</sub> formation. We believe that the rate of H<sub>2</sub> formation from CZ3S supported catalysts is higher because it was reduced (in situ pre-treatment before starting reforming experiment) at lower temperature (400 °C) compared to the CZ7S supported catalysts (500 °C) and therefore, the active metal particles are expected to be less sintered. According to our observations, the H<sub>2</sub> selectivity changes in the order of ZrO<sub>2</sub> ~ CZ7S ~ CZ3S > Alnf and the H<sub>2</sub> activity changes according to the following order: Alnf > ZrO<sub>2</sub> > CZ3S > CZ7S for bimetallic catalysts.

## Conclusions

Novel Ni and Ni–Pt catalysts supported on alumina nano-fibre (Alnf), ZrO<sub>2</sub> and ceria–zirconia–silica (CZ<sub>x</sub>S) were prepared using various methods. The CZ<sub>x</sub>S supports were prepared with 5% ceria and 3–11% silica concentration. The effect of sequence of impregnation and type of support on the reducibility and activity of hydrogen production from aqueous phase reforming of sorbitol was tested. Temperature programmed reduction carried out in this study suggests that the impregnation sequence plays an important role for Alnf supported catalysts. From these results, we conclude that the promoting effect of Pt on Ni reducibility and activity can be greatly inhibited if Ni is impregnated first on Alnf. It is also believed that the sequentially impregnated Pt/Ni/Alnf catalyst did not form Ni–Pt the bi-metallic particles. Ni–Pt alloy formation is desirable because of its synergistic properties and enhanced activity [7, 15]. Bimetallic catalysts supported on ZrO<sub>2</sub> and CZ<sub>x</sub>S supports did not show any effect of sequence of impregnation. The concentration of silica in CZ<sub>x</sub>S support series seems to play an important role for Ni reducibility. It is believed that silica did not form any compound with ceria–zirconia and therefore, silica exists as amorphous layer on the Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> crystals. Ni impregnated on 3% silica concentration (CZ3S) support was reduced at <700 °C. At higher silica concentration ceria and NiO reduction peaks shifted to higher temperatures. The rate of H<sub>2</sub> formation from sorbitol reforming was found to be highest for co-impregnated Ni–Pt/Alnf, followed by ZrO<sub>2</sub> and CZ<sub>x</sub>S supported catalysts.

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