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## Role of the strong Lewis base sites on glucose hydrogenolysis

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Abstract: This work reports the individual role of strong Lewis base sites on catalytic conversion of glucose hydrogenolysis to acetol/lactic acid, including glucose isomerisation to fructose and pyruvaldehyde rearrangement/hydrogenation to acetol/lactic acid.  $La_2O_3$ ,  $Nd_2O_3$ ,  $Sm_2O_3$ , and  $Pr_6O_{11}$  were selected as representative oxides consisting of different base sites. The basicity of these lanthanide oxides was characterised by CO2-TPD and DRIFT spectroscopy. It was found that lanthanide cation-oxygen pairs, Brønsted OH group coordinated with one Lanthanide cation, and lanthanide cation near lanthanide cation-oxygen pairs are the dominant base sites as compared to the other base sites on La2O3, Nd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub>. In addition, the relative concentration of the base sites is different over the examined lanthanide oxides. These unique properties of lanthanide oxides are used to understand the individual role of base sites on the reactions mentioned above. Then, the catalytic results were correlated with the base properties of these lanthanide oxides. Based on this correlation, the base site requirements for each reaction were identified. In this regard, Brønsted OH group coordinated with one Lanthanide cation over Nd<sub>2</sub>O<sub>3</sub> is found to be the suitable base site for glucose isomerisation. On the other hand, lactic acid is produced as the main product in glucose hydrogenolysis over lanthanide cation near lanthanide-oxygen pairs on Pr<sub>6</sub>O<sub>11</sub>. Finally, lanthanide-oxygen pairs over La2O3 are suitable base sites for retro-aldol condensation of fructose to C3 chemicals.

#### Introduction

Glucose is an intermediate platform chemical which can be converted into a wide range of building blocks including sugar alcohols, glycols, acids, and furanic compounds to produce biobased chemicals.<sup>[1]</sup> Particularly, base-catalysed aqueous conversion of glucose to acetol/propylene glycol has received considerable attention.<sup>[2]</sup> This conversion involves a set of parallel and series reactions including glucose isomerisation and pyruvaldehyde hydrogenation/rearrangement.<sup>[3]</sup> Several heterogeneous and homogeneous base catalysts were developed for these reactions.<sup>[2c, 4]</sup> Moreover, heterogeneous base catalysts are preferred over homogeneous ones, mainly due to alkali separation, neutralisation and corrosion issues.<sup>[5]</sup> Furthermore, higher yields of products have been reported over heterogeneous base catalyst compared to the homogeneous ones in some studies.<sup>[6]</sup> For instance, it has been reported that fructose yield upon glucose isomerisation reaches up to 40% using cation-exchanged zeolites, mixed oxides,[6c] and metallosilicates [6b] as heterogeneous catalysts. Besides, catalytic hydrogenolysis of glucose to acetol/propylene glycol in the H<sub>2</sub> atmosphere has also been reported in several studies over heterogeneous catalysts. In this context, supported metal catalysts, promoted by basic oxide have been developed for converting glucose to acetol and propylene glycol <sup>[2a]</sup>. Catalysts such as Cu-La<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>,<sup>[3]</sup> Ni–SnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>,<sup>[7]</sup> Ni/ZnO-CNT <sup>[8]</sup> and Ru/Ac+ZnO <sup>[9]</sup> were developed for this process. In addition, base oxides, such as grafted Sn<sup>IV</sup> onto a mesoporous silica MCM-41, ZrO<sub>2</sub>, and CuCTAB/MgO have been reported to catalyse glucose conversion to lactic acid under inert atmosphere.<sup>[2c]</sup>

In summary, these studies have shown that the key role of the base sites is to convert first glucose to fructose, and then break the carbon bond between the third and fourth carbon at fructose to produce C<sub>3</sub> chemicals.<sup>[3, 10]</sup> However, the individual role of the different base sites is still not well understood. Ohyama et al. reported that glucose isomerisation over alkaline earth metal titanates depends on the base strength and concentration.[6a] They have shown that the base strength of various titanates promoted by alkali and alkali earth metals are different. Similarly, Deng et al. reported that Ni-SnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyses glucose conversion to acetol under H<sub>2</sub> atmosphere.<sup>[7]</sup> Basicity of SnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, CeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, ZnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and AlO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> sample was compared using CO2-TPD. It has been found that the  $SnO_x/Al_2O_3$  sample with the higher concentration of strong base sites is more selective to acetol compared to other oxides examined in that study. Recently, glucose hydrogenolysis to acetol and propylene glycol over Cu-La<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> was reported.<sup>[3]</sup> Catalytic studies and CO2-TPD characterisations revealed that moderate and strong base sites play a vital role in this reaction. The role of the different active components on the product distribution of glucose hydrogenolysis discussed in this study. In summary, copper was an appropriate active metal component for the hydrogenation of the fragments formed after retro-aldol condensation reactions, while lanthanum oxide was providing the base sites for the glucose isomerization and retro-aldol condensation reactions. Similar to other reports, strong base sites played a vital role in the conversion of glucose to propylene glycol. Hence, it is essential to understand the nature and function of the strong base sites in the glucose conversion to fructose and C3 chemicals, including lactic acid and acetol/propylene glycol.

To achieve the aim mentioned above, a series of catalyst systems with distinct base properties is necessary. In this study, lanthanide oxides used as the base promoters. It is worth noting that lanthanum oxide is known to be a suitable base promoter for glucose conversion to fructose <sup>[11]</sup> and C<sub>3</sub> chemicals.<sup>[2a, 3]</sup> Moreover, it has been reported that base properties of lanthanide oxides are attributed to lanthanide contraction.<sup>[12]</sup> Sato et al. have shown that the base strength of the lanthanide oxides decreased by decreasing the radius of the lanthanide

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cation. Inspired by these studies mentioned above, four different lanthanide oxides with distinct strong Lewis base sites are thoroughly characterised and applied in the catalytic conversion of glucose. Indeed, two different active catalyst components, namely Cu/Al<sub>2</sub>O<sub>3</sub> and base sites, are physically mixed. Using this method, the only catalyst variable will be base oxides. Then, the differences in the nature and strength of the base sites over La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, Pr<sub>6</sub>O<sub>11</sub> can be used as an appropriate tool to understand the role of the Lewis base sites on the catalytic conversion of glucose, gaining more insights into the correlation between catalyst properties and the strength of Lewis base sites. Eventually, this approach can be used to guide future catalyst developments for glucose conversion.

#### **Results and Discussion**

#### **XRD** characterisation

Figure 1 shows the XRD patterns of the lanthanide oxides, showing sharp peaks and thereby confirming high crystallinity of the oxides. Pure phases of hexagonal La<sub>2</sub>O<sub>3</sub> (PDF 01-076-7398), hexagonal Nd<sub>2</sub>O<sub>3</sub> (PDF 00-041-1089), cubic Sm<sub>2</sub>O<sub>3</sub> (PDF 03-065-3183), and cubic Pr<sub>6</sub>O<sub>11</sub> (00-042-1121) were obtained by calcination of the corresponding lanthanide nitrate precursors.



Figure 1. XRD spectra of lanthanide oxides.

#### Base properties and surface area

Figure 2 shows the CO<sub>2</sub>-TPD profiles of the lanthanide oxides. Three different desorption peaks can be identified in the CO<sub>2</sub>-TPD profiles. Di Cosimo et al. assigned these peaks to CO<sub>2</sub> adsorbed on base sites over the surface of the oxides.<sup>[13]</sup> According to this study, these peaks can be assigned to hydroxyl groups (100-200 °C), metal–oxygen pairs (300-500 °C), and oxygen anions (>500 °C) on the surface of the oxides. However, the assignment of the surface base pairs to the CO<sub>2</sub>-

TPD signals seems to be more complicated. It has been shown that thermal stability of bidentate and monodentate carbonates could vary from 100 °C to 600 °C.[14] All lanthanide oxides used in this study, possess two peaks in the temperature range between 100 and 400 °C. CO2-TPD profile of the 5%Cu/Al2O3 also possesses two peaks in this temperature range. Besides, CO<sub>2</sub> desorption from La<sub>2</sub>O<sub>3</sub> and Nd<sub>2</sub>O<sub>3</sub> contain the third peak in the temperature range of 450-650 °C. The observed CO2-TPD profiles are in agreement with the ones presented by Sato et al.<sup>[12]</sup> They have shown that rare metal oxides presented different CO<sub>2</sub>-TPD profiles by calcination at 800 °C. Then, the CO2-TPD profiles of the oxides are de-convoluted, and the amount of the desorbed CO<sub>2</sub> is reported in Table 1. As it can be seen, strong base sites dominate on the surface of La<sub>2</sub>O<sub>3</sub>. In contrast, moderate base sites dominate on Nd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, and Pr<sub>6</sub>O<sub>11</sub> and weak base sites dominate on 5%Cu/Al<sub>2</sub>O<sub>3</sub>. Also, low concentration of week base sites is observed over all lanthanide oxides used in this study. The surface area of the oxides is also presented in Table 1. It is worth noting that the BET surface area of  $Sm_2O_3$  is 13.9 m<sup>2</sup>/g, which is almost three folds of that of the other lanthanide oxides.



Figure 2. CO<sub>2</sub>-TPD profile of the lanthanide oxides and 5%Cu/Al<sub>2</sub>O<sub>3</sub>

Table 1	The concentration	of the base	sites and	surface	area of
	the lanthanide	oxides and	5%Cu/Al <sub>2</sub>	O₃.	

Lanthanides	Concentration of base sites, (µmol/m²)			SBET	
	Weak	Moderate	Strong	(m²/g)	
La <sub>2</sub> O <sub>3</sub>	0.6	1.0	2.1	3.9	
$Nd_2O_3$	1.4	6.8	1.2	2.9	
$Sm_2O_3$	1.6	6.2	-	13.9	
Pr <sub>6</sub> O <sub>11</sub>	1.6	4.0	-	3.1	
5%Cu/Al <sub>2</sub> O <sub>3</sub>	0.5	0.1	-	90.5	

## Formation of carbonate species on lanthanide oxides upon CO<sub>2</sub> adsorption

Upon exposure of the lanthanide oxides to CO2 at 30 °C, several peaks appeared in the 2000-1000 cm<sup>-1</sup> region of the FTIR spectra. Then, the physically absorbed CO<sub>2</sub> is desorbed in a flow of He at room temperature, and the resulting spectra are presented in Figures 3-5. Clearly, there are several carbonate species formed on the surface of the lanthanide oxides and 5%Cu/Al<sub>2</sub>O<sub>3</sub>. The structures of the possible carbonate species formed on the surface of the lanthanide oxides are presented in Figure S1. The assignment to the FTIR signals was well established by Sebastián et al.,[13] using previously reported wavenumbers and width band splitting of the adsorbed carbonate species on the base oxides, along with their thermal stabilities to assign the FTIR peaks. The same approach was used by Köck et al. [15] to identify the carbonate species formed on the surface of Yttria-Stabilized ZrO<sub>2</sub> upon CO<sub>2</sub> adsorption. Figure 3 shows the formation of different carbonate species on the surface of the La<sub>2</sub>O<sub>3</sub> and their thermal stability up to 500 °C. The spectrum of the carbonates formed on the surface of the La<sub>2</sub>O<sub>3</sub> was analysed based on the methodology described above, using the FTIR spectra presented in Figure 3 and previous reports. As it can be seen in Figures 3-5, five distinct carbonates can be identified on the surface of lanthanide oxides and 5%Cu/Al<sub>2</sub>O<sub>3</sub>. The presence of these carbonate species on the surface of the lanthanide oxides and 5%Cu/Al<sub>2</sub>O<sub>3</sub> at two different temperatures is summarised in Table S1. The formation of the Bridged and bidentate carbonates demonstrate the presence of the Lewis acid-base pairs (Ln3+-O2-) on the surface of lanthanide oxides.<sup>[13]</sup> Bidentate carbonate species persist up to 300 °C on the IR spectra of La2O3, while these carbonate species are removed under flowing He at 500 °C (Figure 3). Bridge carbonates are easily removed by outgassing the sample up to 150 °C. On the other hand, CO2 adsorb on the Lewis acid sites close to Lewis acid-base pairs (Ln<sup>3+</sup> nearby Ln<sup>3+</sup>-O<sup>2-</sup>) in the form

of polydentate carbonate. Polydentate carbonates are the most stable carbonates formed on the surface of the La<sub>2</sub>O<sub>3</sub> as these species are stable up to 500 °C. Besides, monodentate bicarbonate species reveals the presence of Brønsted OH group coordinated with a Lanthanide cation (Ln<sup>3+</sup>-OH<sup>-</sup>). CO<sub>2</sub> desorbs over this base site by heating up to 500 °C. Finally, carboxylates result from back bonding between d or f orbitals of La3+ ions and the  $\pi^*$  orbitals of a C-O bond of CO<sub>2</sub>. However, these carboxylates are not stable at the temperature higher than 150 °C. Linking the results of CO2-TPD and CO2-DRIFT is not straight forward. It has been shown that different types of monodentate and bidentate carbonates with different thermal stabilities ranging from 100 °C to 600 °C could exist.<sup>[14]</sup> Considering the previous discussion, the first peak of the CO<sub>2</sub>-TPD profile may correspond to hydroxyl groups, carboxylates and bridge carbonates. Moreover, the other two peaks at higher temperature can mainly result from CO<sub>2</sub> desorption from bidentate carbonates, monodentate bicarbonates and polydentate carbonates.



# Figure 3. Infrared spectra collected on La<sub>2</sub>O<sub>3</sub> after desorption of formed carbonates under flowing He upon heating to 500 °C. All peaks are assigned to the corresponding carbonates.

It is clear that the relative concentrations of specific carbonates on the surface of lanthanide oxides and 5%Cu/Al<sub>2</sub>O<sub>3</sub> are different (Figures 4 and 5). As seen in Figure 5, monodentate bicarbonates dominate on the surface of Nd<sub>2</sub>O<sub>3</sub>, while the concentration of polydentate carbonates is lower as compared to the one on the other oxides. In addition, the relevant intensity of bidentate carbonate is lower over Pr<sub>6</sub>O<sub>11</sub> and Nd<sub>2</sub>O<sub>3</sub> as compared to the other carbonates in these oxides. On the other hand, CO<sub>2</sub> adsorbed on the surface of Pr<sub>6</sub>O<sub>11</sub>, Sm<sub>2</sub>O<sub>3</sub>, and 5%Cu/Al<sub>2</sub>O<sub>3</sub> mostly in the form of polydentate carbonates (Figure 4). In next section, the strength of the carbonates over lanthanide oxides and 5%Cu/Al<sub>2</sub>O<sub>3</sub> upon heating to 300 °C will

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be investigated as the focus of this study is to understand the individual effect of the strong Lewis base sites on glucose hydrogenolysis.



Figure 4. Infrared spectra collected on 5%Cu/Al<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> after CO<sub>2</sub> adsorption followed by purging under flowing He at 30 °C.



Figure 5. Infrared spectra collected on Nd<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub> after CO<sub>2</sub> adsorption followed by purging under flowing He at 30  $^{\circ}$ C.

## Strength of the carbonate species formed on the surface of lanthanide oxides

Glucose hydrogenolysis to propylene glycol was reported to be more selective over moderate and strong base sites.<sup>[3, 7]</sup> In addition, the yield of glucose isomerisation to fructose was also shown to be higher over strong base sites.<sup>[6a]</sup> Hence, the strength of the carbonates formed on the lanthanide oxides was analysed by desorbing CO<sub>2</sub> in flowing He at 300 °C to determine the strength of the base sites on the surface of lanthanide oxides. The IR spectra of the carbonates after desorption at 300 °C are depicted in Figures 6 and 7. Similarly to the IR spectra at 30 °C, the distribution of the carbonates over lanthanide oxides and 5%Cu/Al<sub>2</sub>O<sub>3</sub> is different. However, only three carbonate species are present on the surface of the oxides, including monodentate bicarbonate, bidentate carbonate and polydentate carbonate, which are shown in Table S1 as well. The integrated absorbance profiles of the carbonates on the surface of Lanthanide oxides and 5%Cu/Al<sub>2</sub>O<sub>3</sub> after desorption at 300 °C are depicted in Figure 8 to get a clear comparison of the base properties. Polydentate carbonate is the only carbonate present on the surface of Pr<sub>6</sub>O<sub>11</sub>. Furthermore, mainly polydentate carbonate is observed on the surface of Sm<sub>2</sub>O<sub>3</sub> and 5%Cu/Al<sub>2</sub>O<sub>3</sub>. In addition, low concentrations of bidentate carbonates and monodentate bicarbonates on the surface of the Sm2O3 also exist. Nd2O3 contains all three types of carbonates, with the dominance of monodentate bicarbonate. For La2O3, the concentration of bidentate carbonate is the highest among the four lanthanide oxides investigated in this study. In summary, the difference in the distribution of the strong base sites over lanthanide oxides in this study is sufficiently significant to understand the role of the different strong Lewis base sites in glucose hydrogenolysis. More specifically, the individual function of Ln<sup>3+</sup>-O<sup>2-</sup>, Ln<sup>3+</sup>-OH<sup>-</sup>, and Ln<sup>3+</sup>-(Ln<sup>3+</sup>-O<sup>2-</sup>) pairs over La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub> will be correlated with the catalytic results of glucose hydrogenolysis.

As shown by CO<sub>2</sub>-TPD and CO<sub>2</sub>-FTIR studies, the surface of the lanthanide oxides contains weak and strong base sites. Moreover, the type and amount of the strong base sites over the series of lanthanide oxides are different. In following sections, the role of strong Lewis base sites on the catalytic performance is studied. Indeed, it should be noted that cooperative role of weak base sites cannot be ruled out since they are present over all lanthanide oxides.



Figure 6. Infrared spectra collected on Sm\_2O\_3 and La\_2O\_3 after desorption under flowing He at 300  $^\circ\text{C}.$ 

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Figure 7. Infrared spectra collected on 5%Cu/Al<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub> and Pr<sub>5</sub>O<sub>11</sub> after desorption under flowing He at 300 °C.



Figure 8. Integrated absorbance signals of the carbonates on the surface of the Lanthanide oxides and 5%Cu/Al<sub>2</sub>O<sub>3</sub> (after desorption at 300 °C). A<sub>1</sub>: Polydentate carbonates, A<sub>2</sub>: Bidentate carbonates, A<sub>3</sub>: Monodentate bicarbonates, and A: A<sub>1</sub> +A<sub>2</sub> +A<sub>3</sub>

#### Catalytic studies

The catalytic conversion of glucose isomerisation to fructose, pyruvaldehyde hydrogenation/rearrangement to acetol/lactic acid, and glucose hydrogenolysis to acetol/lactic acid were studied, and results are summarised in Figures 9-12.

Glucose isomerisation to fructose has been reported to follow two different mechanisms known as base catalysed, and Lewis acid catalysed isomerisation.<sup>[16]</sup> Sato et al. <sup>[12, 17]</sup> analysed the acid-base properties of lanthanide oxides using CO<sub>2</sub>-TPD and NH<sub>3</sub>-TPD. Based on their analysis, these oxides only possess base sites. To further assure that the glucose isomerisation over these oxides follows proton transfer mechanism catalysed by base sites, an NMR study has been carried out using La<sub>2</sub>O<sub>3</sub> as a base catalyst, following the procedure reported by Román et al.[16] While glucose-D2 is converted to fructose-D1 when glucose isomerisation is catalysed over Lewis acid sites, glucose-D2 is converted to unlabelled fructose when the reaction proceeds over base sites. In this case, unlabelled glucose is produced by reverse isomerisation of the unlabelled fructose. The <sup>1</sup>H NMR spectra of glucose-D2 reacted over La<sub>2</sub>O<sub>3</sub> is presented in Figure S2. <sup>1</sup>H NMR spectra of glucose-D2 and unlabelled glucose are also shown in this Figure. The <sup>1</sup>H NMR spectra of glucose-D2 reacted over La2O3 shows the presence of regular glucose in the reaction solution confirmed by the appearance of the peaks at  $\delta$ =3.1. Hence, it is confirmed that glucose isomerisation over lanthanide oxides is a base catalysed reaction. Moreover, some experiments were designed to check whether the isomerisation reaction is heterogeneously catalysed by lanthanide oxides. In these experiments, the lanthanide oxides were separated from the liquid solution after the catalytic study. Then, the obtained liquid solution is applied in a subsequent isomerisation reaction at 100 °C and 5 bar of N2 for 30 min. No glucose was observed under this condition, showing that the reaction is heterogeneously catalysed by the lanthanide oxides.

As shown in Figure 9, 10% of glucose is converted to fructose over lanthanide oxides at 100 °C after 30 min catalytic reaction under 5 bar of N<sub>2</sub> except for Pr<sub>6</sub>O<sub>11</sub>. Over Pr<sub>6</sub>O<sub>11</sub>, the rate of glucose conversion is higher, reaching 10% only after 10 min catalytic reaction at the same conditions. Glucose isomerisation to fructose is more selective over Nd2O3 than over other lanthanide oxides. Selectivity to fructose reaches 66.5% over Nd<sub>2</sub>O<sub>3</sub>, while a selectivity of only 55.4%, 41.5%, and 43.4 is achieved over La<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, and Pr<sub>6</sub>O<sub>11</sub>, respectively. With all lanthanide oxides, near 7% mannitol and 4% lactic acid are produced as side products along with fructose. It is worth noting that total detected carbon species analysed by HPLC decreases the lanthanides in the following over order. Nd<sub>2</sub>O<sub>3</sub>>La<sub>2</sub>O<sub>3</sub>>Sm<sub>2</sub>O<sub>3</sub>=Pr<sub>6</sub>O<sub>11</sub>. The carbon loss upon glucose conversion in aqueous solution at high temperature is usually ascribed to the formation of Humins and condensation products,<sup>[3, 18]</sup> The first step in the formation of these undesired products was reported to be dehydration reactions of glucose and fructose along with hydrated HMF. Hence, it can be concluded that the existence of Lewis acid sites near base pairs promote the rate of the condensation reaction, resulting in a loss of carbon. Considering the CO2-TPD profile of the lanthanide oxides, the presence of the strong base sites is important to prevent loss of carbon in glucose isomerisation. Interestingly, Nd<sub>2</sub>O<sub>3</sub> that contains less Ln<sup>3+</sup>-(Ln<sup>3+</sup>-O<sup>2-</sup>) sites but more Ln<sup>3+</sup>-OH<sup>-</sup> base sites, yields more fructose compared to the other lanthanides. So, it can be concluded that glucose isomerisation to fructose is more selective over Brønsted OH group coordinated with one Lanthanide cation (Ln<sup>3+</sup>-OH<sup>-</sup>) since these sites are the dominating ones over Nd<sub>2</sub>O<sub>3</sub>. The correlation between different strong Lewis base sites and glucose

isomerisation rate could be useful for developing new catalysts with proper base sites to catalyse this reaction efficiently.

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Figure 9. Glucose isomerisation to Fructose over lanthanide oxides. Reaction condition: 5wt% glucose, 50 ml water, 1 gr catalyst, 100  $^{0}$ C, 5 bar of N<sub>2</sub>, reaction time: 30 min, except for Pr<sub>6</sub>O<sub>11</sub> (10 min)

In addition, pyruvaldehyde hydrogenation/rearrangement over the lanthanide oxides physically mixed with Cu/Al<sub>2</sub>O<sub>3</sub> at 200 °C and 34 bar of H<sub>2</sub> was conducted, and the results are presented in Figure 10. Pyruvaldehyde is the intermediate of glucose hydrogenolysis and can be converted to acetol over metallic copper, and to lactic acid and Humins over acid-base sites under the current reaction conditions.<sup>[3, 19]</sup> As it can be seen in Figure 10, lactic acid is main product for all four base promoters which are physically mixed with 5%Cu/Al<sub>2</sub>O<sub>3</sub>. La<sub>2</sub>O<sub>3</sub> physically mixed with Cu/Al<sub>2</sub>O<sub>3</sub> produces the lowest yield of lactic acid at 40.4% compared to the other lanthanide oxides: 51.8% over Nd<sub>2</sub>O<sub>3</sub>, and 57.0% for both Sm<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub>. However, acetol yield remains the same, 18.0%, for all catalysts in this reaction. The yield of acetol increases to 27.0% using 5%Cu/Al<sub>2</sub>O<sub>3</sub> without base promoters. The reason is that acetol is the hydrogenation product of pyruvaldehyde while lactic acid is the result of pyruvaldehyde rearrangement. Interestingly, the lactic acid yield is high as well over 5%Cu/Al\_2O\_3, 52.1%. This yield is even higher than the yield over  $La_2O_3+5\%Cu/Al_2O_3$ . This reaction result raises the question of the role of lanthanide oxides in the absence of 5%Cu/Al<sub>2</sub>O<sub>3</sub>. To answer this question, pyruvaldehyde rearrangement /hydrogenation was performed at the same condition over lanthanide oxides, and the results are presented in Figure 11. Lactic acid yield is 58.1% over La<sub>2</sub>O<sub>3</sub>, 66.4% over Nd<sub>2</sub>O<sub>3</sub> and 69.6% using Sm<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub>. Moreover, 13.0% of acetol is also produced even in the absence of the 5%Cu/Al<sub>2</sub>O<sub>3</sub>. The same trend for the lactic acid yield is lanthanide observed lanthanide oxides and over oxides+5%Cu/Al<sub>2</sub>O<sub>3</sub>. So, it can be concluded that the conversion of pyruvaldehyde can be catalysed by lanthanide oxides and 5%Cu/Al<sub>2</sub>O<sub>3</sub>. In addition, the detected carbon species vary using

different lanthanide oxides. It is worth noting that detected carbon species using La<sub>2</sub>O<sub>3</sub> is lowest compared to other lanthanide oxides either physically mixed with 5%Cu/Al<sub>2</sub>O<sub>3</sub> or not (Figures 10 and 11). As mentioned before, the carbon loss is due to the Humins formation. Hence, this suggests that the Humins yield is the highest when La<sub>2</sub>O<sub>3</sub> is used as a base promoter in pyruvaldehyde hydrogenation /rearrangement.



Figure 10. Hydrogenation/re-arrangement of pyruvaldehyde over lanthanide oxides physically mixed with 5%Cu/Al<sub>2</sub>O<sub>3</sub>, Reaction condition: 0.3wt% pyruvaldehyde solution, 100ml water, 0.15 gr catalyst (5%Cu/Al<sub>2</sub>O<sub>3</sub>+Lanthanide oxide), 200 °C, 34 bar of H<sub>2</sub> gas, 10 min.



Figure 11. Hydrogenation/re-arrangement of pyruvaldehyde over lanthanide oxides, Reaction condition: 0.3wt% pyruvaldehyde solution, 100ml water, 0.15 gr catalyst, 200 °C, 34 bar of H<sub>2</sub> gas, 10 min.

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The function of Lewis acid-base pairs in condensation and hydrolysis has been well explained in the literature.<sup>[20]</sup> It has been shown that Lewis acid-base pairs catalyse nucleophilic attack of water on the substrate. This reaction is catalysed by the formation of metal cation-substrate bonds. Then, the newly formed bond between the metal cation and the substrate positions the substrate or polarises its electron distribution to catalyse the reaction. This mechanism is accepted by several authors for the conversion of pyruvaldehyde to lactic acid and polyols to glycols over homogeneous or heterogeneous base catalysts.<sup>[19-20, 21]</sup> Similarly, the same approach can be used to understand the reaction mechanism of pyruvaldehyde conversion over base oxides in this study. Based on the proposed reaction mechanisms for pyruvaldehyde conversion to lactic acid [21b, 22] and the catalytic studies in this study, three possible pathways for conversion of the pyruvaldehyde are depicted in Scheme 1. Reaction path I proceed by adsorption of pyruvaldehyde on lanthanide cations adjacent to lanthanideoxygen pairs through both carbonyl groups. Then a water molecule is dissociated over lanthanide-oxygen pairs, and a hydroxyl group is transferred to the activated pyruvaldehyde molecule through a nucleophilic attack followed by a hydride shift to produce lactic acid. On the other hand, the reaction path II and III do not involve the activation of pyruvaldehyde over lanthanide cations. Therefore, one may associate the higher yield of lactic acid over Pr<sub>6</sub>O<sub>11</sub> and Sm<sub>2</sub>O<sub>3</sub> with the high concentration of lanthanide cations adjacent to lanthanideoxygen pairs. Recently, a similar correlation between catalytic properties and pyruvaldehyde rearrangement to lactic acid was proposed by Albuquerque et al.<sup>[19]</sup> These authors have shown that pyruvaldehyde conversion to lactic acid proceeds through activation of pyruvaldehyde molecule over coordinatively unsaturated Zr4+ cations. Then water is dissociated over Zr<sup>4+</sup>-O<sup>2-</sup> pairs, generating terminal OH groups to facilitate the rearrangement reaction. Moreover, they showed that a minimum strength of Lewis acidity is required to activate the pyruvaldehyde molecule over acid sites. Therefore, the reaction path I may not occur in the conversion of the pyruvaldehyde over lanthanide oxides as these oxides do not possess Lewis acidity.<sup>[12, 17]</sup> Thus another explanation for the different yields of lactic acid over lanthanide oxides is required. It is shown that La<sub>2</sub>O<sub>3</sub> contains the higher concentration of lanthanide-oxygen pairs. As discussed above, these base sites participate in both lactic acid production and Humins formation. So, the reason for different lactic acid yields over lanthanide oxides might be mostly related to the formation of Humins over Ln3+-O2- pairs. In summary, pyruvaldehyde is converted to lactic acid and acetol over lanthanide oxides under the reaction conditions. However, the presence of strong base sites known as Ln<sup>3+</sup>-O<sup>2-</sup> pairs over La<sub>2</sub>O<sub>3</sub> is decreasing the detected carbon species by 10-15 % via Humins formation.



Scheme 1. Possible reaction pathways of pyruvaldehyde rearrangement to lactic acid and Humins over base sites

Finally, the role of the strong Lewis base sites on glucose hydrogenolysis was investigated. Glucose hydrogenolysis consists of cascade reactions which are catalysed over base sites except for the hydrogenation of the glucose and the formed fragments. These hydrogenation reactions are catalysed over 5%Cu/Al<sub>2</sub>O<sub>3.[3]</sub> Glucose hydrogenolysis over lanthanide oxides physically mixed with Cu/Al<sub>2</sub>O<sub>3</sub> was carried out at the reaction conditions reported in Figure 12. Sorbitol and HMF are produced with yields of 6.6% and 7.5% using 5%Cu/Al<sub>2</sub>O<sub>3</sub>. The yields of these products are less than 1.5% when lanthanide oxides are used as base promoters. It was reported in the literature that aluminium is not an active element in glucose hydrogenolysis.<sup>[2a]</sup> However, acetol and lactic acid are produced with a total yield of 14.4% using 5%Cu/Al<sub>2</sub>O<sub>3</sub>. This can be explained by the base properties of 5%Cu/Al<sub>2</sub>O<sub>3</sub> confirmed by CO<sub>2</sub>-DRIFT and TPD measurements in this work. Indeed, Al3+-(Al3+-O2-) pairs and Al3+-O<sup>2-</sup> pairs are strong base sites. The lower yield of C<sub>3</sub> chemicals over 5%Cu/Al<sub>2</sub>O<sub>3</sub> can be related to the lower concentration of base sites over this catalyst; confirmed by CO2-TPD, or the presence of acid sites. These two parameters cause the increase in the sorbitol and HMF yield; respectively, decreasing the yield of C<sub>3</sub> chemicals.<sup>[3]</sup> As it can be seen in Figure 12, acetol is the main product over La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub> and Sm<sub>2</sub>O<sub>3</sub>, while lactic acid is the dominant product over Pr<sub>6</sub>O<sub>11</sub>. The yield of acetol decreased from 40.1% to 36.5%, 29.5%, and 21.7% when La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, and Pr<sub>6</sub>O<sub>11</sub> are used as base promoters. respectively. On the contrary, the yield of lactic acid increased from 18.8% to 27.6% over these oxides. It was mentioned by several authors that addition of base promotors to supported metals cause an increase in the yield of lactic acid during glucose hydrogenolysis.<sup>[2a, 3, 7, 23]</sup> Herein, we have shown that the type of strong Lewis base sites is changing the yield of lactic acid. The higher yield of lactic acid over Sm<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub> can be explained considering the base properties of these oxides discussed in the previous section. However, the yield of lactic acid over these two oxides is not the same. This difference can be explained by the rate of glucose isomerisation reaction over these two oxides. It is worth noting that reaction rate of glucose isomerisation over Pr<sub>6</sub>O<sub>11</sub> is higher than other oxides. So, pyruvaldehyde is produced in the reaction medium of glucose hydrogenolysis at lower temperatures during the reactor heat-up over this oxide. Then, lactic acid is produced in higher yield as its formation is favoured at lower temperatures compared to acetol. It is important to mention that Nd<sub>2</sub>O<sub>3</sub> is more selective to fructose during glucose isomerisation as compared to La<sub>2</sub>O<sub>3</sub>, and Humins formation was higher over La2O3 Thus, one may expect to produce more acetol upon glucose hydrogenolysis over this oxide. However, the yield of acetol and lactic acid are the same over these two oxides during glucose hydrogenolysis as it can be seen in Figure 12. We can conclude that La<sub>2</sub>O<sub>3</sub> is more selective in the C<sub>3</sub>-C<sub>4</sub> bond cleavage of fructose compared to Nd<sub>2</sub>O<sub>3</sub>. It means that Ln<sup>3+</sup>-O<sup>2-</sup> base pairs are suitable base sites for C<sub>3</sub>-C<sub>4</sub> bond cleavage of fructose. This could explain why similar catalytic results are obtained during glucose

hydrogenolysis over both La<sub>2</sub>O<sub>3</sub> and Nd<sub>2</sub>O<sub>3</sub>. Moreover, similar results over these two oxides during glucose hydrogenolysis shows that lanthanide-oxygen pairs over La<sub>2</sub>O<sub>3</sub> and Brønsted OH group coordinated with one Lanthanide cation over Nd<sub>2</sub>O<sub>3</sub> are suitable base sites for this reaction. Interestingly, both oxides have a third peak in their CO<sub>2</sub>-TPD profiles, indicating the vital role of the strong base sites in this conversion in line with previous reports.<sup>[3, 7]</sup>



 Figure 12. Glucose hydrogenolysis over lanthanide oxides and 5%Cu/Al<sub>2</sub>O<sub>3</sub>, Reaction condition: 0.3wt% glucose, 100 ml water, 0.15 gr catalyst (5%Cu/Al<sub>2</sub>O<sub>3</sub>+Lanthanide oxide), 200 °C, 34 bar of H<sub>2</sub> gas, 10 min, Others: Fructose, Sorbitol, Arabitol, Erythritol, Pyruvaldehyde, Glycerol, Ethylene glycol, 1,2-BDO, HMF.

#### Conclusions

In this study, the individual effect of strong base sites on glucose isomerisation to fructose, pyruvaldehyde rearrangement /hydrogenation, and glucose hydrogenolysis to acetol/lactic acid was investigated. Four different lanthanide oxides with distinct strong base sites were characterised and applied in the mentioned reactions. The results show that different types of base sites catalyse different reactions. More specifically, glucose isomerisation to fructose is more selective over Brønsted OH group coordinated with one Lanthanide cation (Ln<sup>3+</sup>-OH<sup>-</sup>). The presence of lanthanide cations near lanthanide-oxygen pairs catalyses glucose isomerisation along with condensation reactions, resulting in Humins formation. Moreover, lanthanideoxygen pairs catalyse the unwanted side reactions, lowering down the detected carbon species in pyruvaldehyde hydrogenation/rearrangement. On the other hand, lanthanide cation adjacent to lanthanide-oxygen base pairs are more selective towards lactic acid during pyruvaldehyde hydrogenation/rearrangement. Finally, acetol is the primary product of glucose hydrogenolysis when lanthanide-oxygen pairs and Brønsted OH group coordinated with one Lanthanide

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#### **Experimental Section**

#### Catalyst preparation

Nitrate precursors of Lanthanum, Praseodymium, Neodymium, and Samarium were purchased from Sigma-Aldrich. The lanthanide oxides were prepared by decomposing the nitrate precursors in the air at 800 °C with a ramping rate of 2 °C/min for 2 hours. 5% Cu/Al<sub>2</sub>O<sub>3</sub> was prepared by wet impregnation. The appropriate amount of copper nitrate precursor and gamma-alumina were added into a beaker containing 50 ml of water and stirred overnight at room temperature. The resulting powder was dried at 100 °C in a vacuum oven overnight. Then the dried catalyst was calcined at 400 °C for 5 hours using a heating rate of 1°C /min under air flow. The obtained catalyst was reduced in flowing H<sub>2</sub> at 400 °C for 2 hours using heating rate of 2 °C/min. Then, the reduced catalyst was passivated under a flow of 1% O<sub>2</sub> in N<sub>2</sub> for 30 min at ambient temperature before exposing to air. The prepared catalysts were stored in a glove box with N<sub>2</sub> atmosphere prior to catalytic studies.

#### Catalytic activity

The hydrogenolysis of glucose and pyruvaldehyde hydrogenation/ rearrangement were carried out at 200 °C and 34 bar of H<sub>2</sub> in a 300 ml Teflon-lined Parr-reactor. 100 ml of 0.3wt% feed solution was used in these experiments. 0.15 g of a physical mixture of  $5\% Cu/Al_2O_3$  and lanthanide oxide was used as the catalyst in these studies. The amount of 5%Cu/Al<sub>2</sub>O<sub>3</sub> was kept at 0.1 g for all reactions. Catalytic isomerisation of 10wt% glucose to fructose was performed at 100 °C and 5 bar of N<sub>2</sub>. 50 ml of 10wt% glucose solution was used during isomerisation reaction, using 1g of lanthanide oxides as a catalyst. First, high pressure H<sub>2</sub>/N<sub>2</sub> was introduced in the reactor, and then the temperature was increased up to the reaction temperature. The heating time from room temperature to 200 °C and 100 °C were 35 min and 25 min, respectively. Time zero was taken at this point. The resulting solution was collected after cooling down the reactor to room temperature and analysed with HPLC. The equations used to calculate conversion, selectivity and detected carbon species are presented below. HPLC was performed using a 0.5 mM aqueous solution of sulfuric acid as a mobile phase, at a flow rate of 0.5 ml/min. Aminex HPX-87H column was used as separation column operating at 60 °C.



#### Catalyst characterisation

X-ray diffraction patterns (XRD) of the Lanthanide oxides were recorded on a Bruker AXS D8 diffractometer using CuKa radiation employing tube voltage and current of 40 kV and 40 mA, respectively. The Brunauer Emmett Teller (BET)-surface area of the lanthanide oxides was analysed using a Micromeritics ASAP 2420 system. The samples were pre-treated at 200 °C for 2 hours under vacuum and then subjected to N2 physical adsorption at liquid N2 temperature. CO2 temperature programmed desorption (CO<sub>2</sub>-TPD) was used to determine the basicity of the lanthanide oxides. Before analysis, the lanthanide oxides were pretreated in 30 ml/min flow of Ar at 500 °C for 1 hour with a heating rate of 10 °C/min. Then the oxides were cooled down to 30 °C and saturated with CO2 using 30 ml/min flow of pure CO<sub>2</sub> for 30 min. Subsequently, the oxides were treated in a flowing N2 for 30 min at room temperature to remove the physically adsorbed CO2. Finally, CO2-TPD was carried out by heating up the TPD chamber to 800 °C in 30 ml/min flow of He with a heating rate of 10 °C/min. The desorbed CO2 was analysed using a TCD, and the TPD profiles were recorded. For all base oxides, a blank CO2-TPD experiment was carried out without adsorbing CO2. Then the resulting spectra were subtracted from the CO2-TPD profiles of the base oxides. The CO2-TPD profiles were deconvoluted, and the area under the peaks was calculated. CO2-FTIR was carried out to evaluate the base sites and the base strength of the lanthanide oxides. The spectroscopic analysis was carried out on a Frontier MIR (PerkinElmer) equipped with a mercury-cadmium-telluride (MCT) detector, following the procedure described elsewhere.<sup>[24]</sup> In a typical measurement, the sample powder was first placed in a high-pressure cell fitted with ZnSe windows. Before analysis, all samples were pre-treated at 500 °C in flowing Ar (30 ml/min) during 1 hour. Then the samples were cooled down to 30 °C. The spectra of the samples after pre-treatment were taken and used as background. After that, the pre-treated oxides were saturated in 30 ml/min flow of pure CO2 for 30 min. Subsequently, physically adsorbed CO2 was removed from the samples using a 10 ml/min flow of He for 30 min. The samples were then heated up to different temperatures between 100 °C to 300 °C in flowing He at 10 ml/min, and the spectra were recorded after cooling down to room temperature with a resolution of 4 cm<sup>-1</sup>, recording 64 scans. The IR bands are integrated after deconvolution of the IR signals using Gaussian functions. NMR spectra were taken using a Bruker 400 MHz NMR spectrometer. Deuterated glucose at the C2 position was used in the isomerisation reaction to fructose. Then, the reaction solution was separated from catalyst using a centrifuge. The obtained solution was dried in a vacuum oven at 40 °C. The remaining powder was dissolved in 1 ml of D<sub>2</sub>O. Then, <sup>1</sup>H NMR spectra of the glucose-D2 before and after catalytic reactions were analysed to understand the mechanism of glucose isomerisation to fructose, based on the procedure reported elsewhere.[6a]

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