Article

The Effect of Mg and Zn Dopants on Pt/Al₂O₃ for the Dehydrogenation of Perhydrodibenzyltoluene

Rudaviro Garidzirai ¹ , Phillimon Modisha ^{1,*}, Innocent Shuro ², Jacobus Visagie ³, Pieter van Helden ³ and Dmitri Bessarabov ^{1,*}

¹ HySA Infrastructure Centre of Competence, Faculty of Engineering, Potchefstroom Campus, North-West University, Private Bag X6001, Potchefstroom 2520, South Africa; 31831435@nwu.ac.za

² Centre for Chemical Resource and Beneficiation, Faculty of Natural and Agricultural Science, Potchefstroom Campus, North-West University, Private Bag X6001, Potchefstroom 2520, South Africa; Innocent.Shuro@nwu.ac.za

³ Sasol, Group Technology, 1 Klasie Havenga Road, Sasolburg 1947, South Africa; Jacobus.Visagie@sasol.com (J.V.); pieter.vanhelden@sasol.com (P.v.H.)

* Correspondence: phillimon.modisha@nwu.ac.za (P.M.); dmitri.bessarabov@nwu.ac.za (D.B.); Tel.: +27-18-285-2460 (D.B.)

Abstract: The effects of Mg and Zn dopants on the catalytic performance of Pt/Al₂O₃ catalyst were investigated for dehydrogenation of perhydrodibenzyltoluene (H18-DBT) as a liquid organic hydrogen carrier. Al₂O₃ supports were modified with Mg and Zn to produce Mg-Al₂O₃ and Zn-Al₂O₃ with a target loading of 3.8 wt.% for dopants. The modified supports were impregnated with chloroplatinic acid solution to produce the catalysts Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ of 0.5 wt.% Pt loading. Thereafter, the catalysts were characterised using inductively coupled plasma-optical emission spectrometry, scanning electron microscopy-energy dispersive X-ray spectroscopy, hydrogen temperature-programmed reduction, carbon-monoxide pulse chemisorption, ammonia temperature-programmed desorption, X-ray diffraction and transmission electron microscopy. The dehydrogenation experiments were performed using a horizontal plug flow reactor system and the catalyst time-on-stream was 22 h. Pt/Mg-Al₂O₃ showed the highest average hydrogen flowrate of 29 nL/h, while an average of 27 nL/h was obtained for both Pt/Al₂O₃ and Pt/Zn-Al₂O₃. This has resulted in a hydrogen yield of 80% for Pt/Mg-Al₂O₃, 71% for Pt/Zn-Al₂O₃ and 73% for Pt/Al₂O₃. In addition, the conversion of H18-DBT ranges from 99% to 92%, Pt 97–90% and 96–90% for Pt/Mg-Al₂O₃, Pt/Zn-Al₂O₃ and Pt/Al₂O₃, respectively. Following the latter catalyst order, the selectivity to dibenzyltoluene (H0-DBT) ranges from 78% to 57%, 75–51% and 71–45%. Therefore, Pt/Mg-Al₂O₃ showed improved catalytic performance towards dehydrogenation of H18-DBT.

Keywords: liquid organic hydrogen carriers; dibenzyltoluene; dehydrogenation; dopants; by-products

Citation: Garidzirai, R.; Modisha, P.; Shuro, I.; Visagie, J.; van Helden, P.; Bessarabov, D. The Effect of Mg and Zn Dopants on Pt/Al₂O₃ for the Dehydrogenation of Perhydrodibenzyltoluene. *Catalysts* **2021**, *11*, 490. <https://doi.org/10.3390/catal11040490>

Academic Editor: Changzhi Li

Received: 5 March 2021

Accepted: 30 March 2021

Published: 12 April 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Dibenzyltoluene (H0-DBT) is known as one of the most promising liquid organic hydrogen carrier (LOHC) molecules due to its competitive hydrogen storage properties reported in the literature [1–4]. Remarkably, the infrastructure for fuel can be repurposed for storage and transportation of dibenzyltoluene-based LOHC at ambient conditions, because it has diesel-like properties. Hence, the application of dibenzyltoluene for reversible hydrogen storage has reached the commercial stage. However, it is important to further develop the highly active and stable catalysts with minimum by-product formation for the recyclability of the LOHC molecule. It is for this reason that we first discuss literature work, where the catalytic performance was improved by modification of the catalyst with Mg and Zn. Arguably, Pt/Al₂O₃ is the catalyst of choice for dehydrogenation of LOHC molecules. Modification of the Al₂O₃ support using Mg and Zn has been reported to enhance catalytic performance, strengthen metal–support interaction, change support acidity and improve

metal dispersion [5–8]. For example, Zn modification on both Pt/Al₂O₃ and Pt/ZSM-5 catalysts showed improved catalytic performance for propane dehydrogenation [7–10].

Mg-doped Al₂O₃ also has excellent attributes, such as the ability to promote surface diffusion and prevent clustering/sintering by suppressing grain growth [6,11]. Some patents filed in the U.S. also confirm the catalyst improvement upon modification of alumina support with Mg [12–14]. In this case, Mg-modified alumina resisted sintering and agglomeration of the catalyst particles during production of syngas from light hydrocarbons [12]. The challenge is that optimum quantity of Mg is required because too much or too little amounts could have little effect, no effect or negative effect on the catalytic performance [15–17]. For example, Zhang et al. [18] investigated the dehydrogenation of iso-butane using PtSnMgK/Al₂O₃ with different Mg loadings (0.2–0.8 wt.%). The amount of 0.4 wt.% Mg decreased carbon deposition on catalysts, with increased reaction activity and stability. A further increase to 0.8 wt.% Mg drastically decreased both Pt dispersion and catalytic activity. Moreover, Arnby et al. [19] and Zhan et al. [20] also reported the same phenomena for Pt/Al₂O₃ and Pd/Al₂O₃ catalysts, respectively. Auer et al. [21] investigated the effect of trace amounts of sulphur on Pt/Al₂O₃ in the dehydrogenation of H18-DBT and found that 0.25 wt.% S improved the catalytic activity and reduced the formation of high boiling point by-products.

It is reported that Mg does not only reduce the acidity of Al₂O₃ support, but it also lowers the carbon deposition, which is known for catalyst deactivation [22–24]. Since the acidity of Al₂O₃ support could contribute to C–C cleavage of the hydrocarbon molecule [25], therefore the by-products produced from dehydrogenation of H18-DBT [26] could be a result of this. Based on the improvements reported in the literature, modification of the Al₂O₃ support is expected to change the chemical properties of the catalyst and to improve the catalytic performance. This could be a rewarding approach because the commonly used Pt/Al₂O₃ catalyst suffers from deactivation, which results in low catalytic activity for dehydrogenation of H18-DBT. In this work, we investigate the effect of Mg and Zn dopants on Pt/Al₂O₃ catalyst for the dehydrogenation of H18-DBT. This is done by first modifying the Al₂O₃ support using Mg and Zn precursors, followed by impregnation of Pt on the support. The catalysts are further characterised to determine the effect of modification on the physical and chemical properties.

2. Results and Discussion

2.1. Catalytic Dehydrogenation Activity

It has been previously reported that dehydrogenation of H18-DBT follows the order H18-DBT-3H₂ → H12-DBT-3H₂ → H6-DBT-3H₂ → H0-DBT [25], as shown by Scheme 1. Where, H6-DBT and H12-DBT could be regarded as stable intermediates or partially dehydrogenated LOHCs. Dehydrogenation experiments are carried out to compare the performance of the various catalysts (Pt/Al₂O₃, Pt/Zn-Al₂O₃ and Pt/Mg-Al₂O₃) which were allowed to run for 22 h at constant reaction temperature. For all experiments, the weight hourly space velocity (WHSV) is 0.61 h^{−1}. Figure 1 shows hydrogen flow rate (HFR) vs. catalyst time-on-stream for the dehydrogenation of H18-DBT. The Pt/Mg-Al₂O₃ catalyst had the highest initial HFR of 33 nL/h. Other catalysts (Pt/Al₂O₃ and Pt/Zn-Al₂O₃) had a similar initial HFR, 31 nL/h. For the first 12 h, the HFR was not stable, but after 13 h, the catalysts exhibited some stability (particularly Pt/Zn-Al₂O₃). However, in the cases of Pt/Zn-Al₂O₃ and Pt/Al₂O₃, the HFR decreased from 31 to ~24 nL/h. Overall, the Pt/Mg-Al₂O₃ catalyst had the highest activity and stability over a period of 22 h, and the HFR decreased from 33 to 26 nL/h. A similar trend was observed in Figure 2, where catalyst productivity is plotted against time-on-stream. A productivity of 0.1 gH₂/g_{Pt}/min was observed for all catalysts. Furthermore, all catalysts here showed a declining trend in hydrogen yield over a period of 22 h, see Figure 2. The Pt/Mg-Al₂O₃ hydrogen yield decreased from 80% to 60%, whereas the Pt/Al₂O₃ and Pt/Zn-Al₂O₃ hydrogen yields decreased from 72% to 50% and 73–51%, respectively. Therefore, Pt/Mg-Al₂O₃ improved the activity of un-doped Pt/Al₂O₃.

Scheme 1. The reaction pathway for dehydrogenation of perhydrodibenzyltoluene (H18-DBT).

Figure 1. Hydrogen flow rate vs. time-on-stream for dehydrogenation of H18-DBT over 22 h. Reaction parameters: Pt loading 0.5 wt.%, H18-DBT degree of hydrogenation (doh) 99.6%, reaction temperature 300 °C, feed flow 1.3 mL/min, catalyst mass 110 g, weight hourly space velocity 0.61 h^{−1}.

Figure 3 shows the H18-DBT conversion over Pt/Al₂O₃, Pt/Zn-Al₂O₃ and Pt/Mg-Al₂O₃, determined using single quadrupole mass spectrometer (GC-SQ-MS). During the dehydrogenation of H18-DBT, the intermediates H12-DBT and H6-DBT are formed, and they then also become dehydrogenated, until H0-DBT is the only product present. The conversion vs. time-on-stream plot in Figure 3 is based on the amount of H18-DBT present after the reaction. The catalyst Pt/Mg-Al₂O₃ had the highest initial conversion of 99%, followed by the Pt/Zn-Al₂O₃ and Pt/Al₂O₃ catalysts, with 97% and 96% conversions, respectively. After 22 h, the Pt/Mg-Al₂O₃ catalyst still exhibited a stable conversion of 92%, whilst the other catalysts exhibited slightly lower conversions. It is a fact that Mg improves reduction of Pt-oxide and this has led to higher metallic Pt concentration (active sites) on Pt/Mg-Al₂O₃ than that on Pt/Al₂O₃ and Pt/Zn-Al₂O₃ [18]. It is also known that Mg could increase the rate of Al₂O₃ grain densification by raising the diffusion coefficient [11]. Therefore, the larger the grain size, the larger the pores. This has an effect on minimizing the pore diffusion limitation. Hence, improved H18-DBT conversion is observed. As shown in Figure 3, the conversion difference between Pt/Al₂O₃ and Pt/Zn-Al₂O₃ catalyst is not that significant. Further optimisation of Zn loading could result in improved H18-DBT conversion.

Figure 2. Catalyst productivity and hydrogen yield vs. time-on-stream for dehydrogenation of H18-DBT over 22 h. Reaction parameters: Pt loading 0.5 wt.%, H18-DBT doh 99.6%, reaction temperature 300 °C, feed flow 1.3 mL/min, catalyst mass 110 g, weight hourly space velocity 0.61 h^{−1}.

Figure 3. Conversion of H18-DBT vs. time-on-stream over 22 h of dehydrogenation. Reaction parameters: Pt loading 0.5 wt.%, H18-DBT doh 99.6%, reaction temperature 300 °C, feed flow 1.3 mL/min, catalyst mass 110 g, weight hourly space velocity 0.61 h^{−1}.

Figure 4 shows the selectivity of catalysts towards H0-DBT, determined using GC-SQ-MS. The initial selectivity of Pt/Mg-Al₂O₃, Pt/Zn-Al₂O₃ and Pt/Al₂O₃ towards H0-DBT was 78%, 75% and 71%, respectively. Pt/Al₂O₃ was the least selective catalyst here, with a final selectivity of 45%, whereas Pt/Mg-Al₂O₃ was the most selective catalyst, with a final selectivity of 57%, after 22 h. It appeared that a less acidic catalyst favoured dehydrogenation and increased the selectivity, compared with highly acidic supports. Acidic sites of the support facilitate C–C breaking, and as a result, carbon becomes deposited on the catalyst surface [18]. Therefore, lowering the acidity of the support minimizes side reactions (C–C cracking). Thus, the high selectivity could be attributed to an effect of Mg to the adsorption of H0-DBT on the Pt surface and promoting the H0-DBT desorption.

Figure 4 also shows the selectivity of catalysts towards the intermediates: H12-DBT and H6-DBT. All catalysts here showed a decline in selectivity towards H0-DBT, but an increase towards the H6-DBT and H12-DBT intermediates. The decline in selectivity over time is due to the catalyst instability. Pt/Al₂O₃ selectivity towards H6-DBT increased from 24% to 39%, while that of H12-DBT increased from 5% to 10%. This is an indication that catalyst active sites are compromised by deactivation and over time, H6-DBT and H12-DBT become difficult to be dehydrogenated.

Figure 5 shows the total by-products formed during the dehydrogenation of H18-DBT. In the dehydrogenation of H18-DBT, the higher the catalytic activity, the more by-products are produced. These by-products are a combination of high- and low-boiling-point compounds [26]. Pt/Mg-Al₂O₃ showed the highest initial concentration of by-products (6.8 mol%), followed by Pt/Zn-Al₂O₃ (5.3 mol%) and Pt/Al₂O₃ (4.2 mol%). After 22 h, Pt/Mg-Al₂O₃ still produced the highest concentration of by-products (3.2 mol%). Despite the fact that Pt/Mg-Al₂O₃ is less acidic, a highly active catalyst produces more by-products because the Pt active sites promote C–C breaking by hydrogenolysis. Bocanegra et al. [27] have reported that Pt/MgAl₂O₄ has higher hydrogenolytic capacity than Pt/Zn-Al₂O₄.

The deactivation parameter, $\Delta X = (X_i - X_f)/X_i \times 100$, is calculated to determine the % deactivation over a reaction period of 22 h. Table 1 summarises the performance of the catalysts for dehydrogenation of H18-DBT. Pt/Mg-Al₂O₃ catalyst has the lowest deactivation parameter ($\Delta X = 6.1\%$) compared to Pt/Al₂O₃ ($\Delta X = 7.2\%$) and Pt/Zn-Al₂O₃ ($\Delta X = 7.3\%$). This is an indication of improvement as Mg-doped catalyst deactivation is lesser. Increasing the Mg loading could lower the deactivation parameter and thus improve the catalyst stability further. Bai and co-workers reported the same phenomena for Mg-doped PtSnNa/ZSM-5, where the deactivation parameter decreased from 10% to 7% [22].

Table 1. Summary of catalysts' performance for dehydrogenation of H18-DBT.

Catalyst	X _i	X _f	S _i	S _f	Y _i	Y _f	ΔX
Pt/Al ₂ O ₃	97	90	71	45	72	49	7.2
Pt/Mg-Al ₂ O ₃	99	93	77	57	80	60	6.1
Pt/Zn-Al ₂ O ₃	96	89	74	51	73	51	7.3

X_i and X_f = initial and final conversion (%), S_i and S_f = initial and final selectivity (%), Y_i and Y_f = initial and final yield (%), ΔX = deactivation parameter (%).

Figure 4. Selectivity of the catalysts to H0-DBT, H6-DBT and H12 DBT over 22 h time-on-stream. Reaction parameters: Pt loading 0.5 wt.%, H18-DBT doh 99.6%, reaction temperature 300 °C, feed flow 1.3 mL/min, catalyst mass 110 g, weight hourly space velocity 0.61 h^{−1}.

Figure 5. Amounts of by-products obtained over 22 h of catalyst time-on-stream. Reaction parameters: Pt loading 0.5 wt.%, H18-DBT doh 99.6%, reaction temperature 300 °C, feed flow 1.3 mL/min, catalyst mass 110 g, weight hourly space velocity 0.61 h^{−1}.

2.2. Characterisation

The subsections below describe the results of experiments and procedures carried out to determine the following: Pt loading, catalyst composition, metal dispersion, metal reducibility, catalyst acidity, particle size distribution and the source of LOHC by-products.

2.2.1. Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS)

The target Pt loading for all catalysts was 0.5 wt. % Pt. The actual loadings confirmed by ICP-OES for Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ were 0.48, 0.49 and 0.48 wt.%, respectively (see Table 2). The target loading of Mg and Zn was 3.8 wt.%—the actual loadings were 3.89 and 3.44 wt.%, respectively.

Table 2. Metal loadings and elemental composition of the catalysts determined using inductively coupled plasma-optical emission spectrometry (ICP-OES).

Catalyst	Target Pt Loading (wt.%)	Actual Loading (wt.%)		
		Pt	Mg	Zn
Pt/Al ₂ O ₃	0.5	0.48	-	-
Pt/Mg-Al ₂ O ₃	0.5	0.49	3.89	-
Pt/Zn-Al ₂ O ₃	0.5	0.48	-	3.44

SEM-EDS confirmed the presence of Pt, Mg and Zn in the reduced catalysts, as shown in Figure 6. Elemental line analysis indicated that the Mg-doped catalyst has the greatest amount of Pt distributed throughout the pellet. The Zn-doped and undoped catalysts exhibited an eggshell type of catalyst, where there is much Pt on the edges and little inside (<0.1% Pt). It is possible that Mg promotes the diffusion of the precursor solution during impregnation, hence Pt is distributed throughout the support. This is also consistent with the image in Figure 6, where the cross-sections of the pellets shows Pt distribution.

Figure 6. Elemental line scan analysis showing Pt distribution at 40-micron equidistance.

2.2.2. Hydrogen Temperature-Programmed Reduction (H₂-TPR)

H₂-TPR profiles showed broad and intense peaks at temperatures between 100 and 200 °C and small peaks at temperatures between 300 and 500 °C (see Figure 7). The first broad peaks were due to the reduction of PtO and PtO₂ species weakly bonded to the surface of the support [28]. The second peak indicated strong support interaction with Pt, possibly leading to the formation of PtAl₂O₄ spinel species (formed during impregnation and calcination), which are difficult to reduce. It is interesting to note that the second peaks of the Mg- and Zn-doped Pt/Al₂O₃ shifted to higher temperatures, indicating the presence of stronger interactions with the support. Therefore, doped catalysts have stronger metal support interactions than non-doped Pt/Al₂O₃. This is known to prevent sintering of particles [6,7,11]. Furthermore, Kumar et al. [17] ascribed the increase or shift in reduction temperature of the Mg-doped catalyst to the weak electronegative bond between Mg and O₂ in MgO, which causes the oxygen to preferably bond with Pt. Another possible reason could be the formation of Mg and Zn aluminates, which increase the reduction temperature. The following hydrogen consumptions for Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ were observed: 34, 64 and 55 µmol/g, respectively. The hydrogen consumption of 34 µmol/g for Pt/Al₂O₃ is close to the theoretical value (30.3 µmol/g) reported for the complete reduction of Pt⁴⁺ to Pt⁰ [29]. However, the consumption of Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ is higher than the stoichiometric value for reducing all platinum species. This increment could be possibly due to the reduction of impurities on the support [15,29].

Figure 7. Hydrogen temperature-programmed reduction (H_2 -TPR) profiles of the calcined catalysts.

2.2.3. CO Pulse Chemisorption

The addition of Mg and Zn dopants decreased the dispersion of Pt particles (see Table 3). A decrease in the metallic surface area and the formation of strongly bonded Pt complexes with doped Mg and Zn supports may have contributed to this. Strong metal–support interactions make it difficult for CO to absorb onto Pt due to fewer exposed active sites. There are, however, several reports that describe an increase in dispersion upon Mg doping [6,17]. Low dispersion of 34% for Pt/Mg- Al_2O_3 compared to 38% for Pt/ Al_2O_3 can be ascribed to alteration of the adsorptive properties of Pt/Mg- Al_2O_3 when Pt reacts with basic sites of Mg [15,30]. Pt/Zn- Al_2O_3 had the lowest Pt dispersion, 23%, relatively close to values reported in the literature [17,31,32].

Table 3. TPR and CO pulse chemisorption of the catalysts.

Catalyst	Pt Dispersion, %	Active Particle Diameter, nm	Metallic Surface Area, m^2/g sample	H_2 Consumption, $\mu mol/g$
Pt/ Al_2O_3	38	3.0	0.47	34
Pt/Mg- Al_2O_3	34	3.3	0.42	64
Pt/Zn- Al_2O_3	23	5.0	0.28	55

This could be due to the formation of Pt-Zn alloys and strong interactions that may not be active in CO chemisorption [29]. The elemental line scan in Figure 6 shows high Pt distribution throughout the Mg-doped catalyst (not an eggshell type) as opposed to the surface dispersion of Pt shown in Table 3.

2.2.4. NH_3 -TPD

NH_3 -TPD results are shown in Figure 8, including desorption profiles (dotted lines) and their respective deconvoluted peaks (solid lines) for the Al_2O_3 supports and Pt/ Al_2O_3 catalysts. The first peak was at 200–250 °C and the second peak at 550–700 °C. The peaks are attributed to desorption of NH_3 due to weak/intermediate acidic sites and strong acidic sites, which appear in the region of 200–400 °C and 400–550 °C respectively, for γ - Al_2O_3 [33–36]. Values for the acidity of supports and catalysts, determined by NH_3 -TPD, are tabulated in Table 4. Results show that Mg doping decreased the total acidity of Al_2O_3 from 0.63 to 0.40 mmol NH_3/g , while Zn doping slightly increased it to 0.68 mmol NH_3/g . The order of the total acidity of supports was Zn- Al_2O_3 > Al_2O_3 > Mg- Al_2O_3 . The addition of Mg decreased the total acidity of alumina by 37%, whereas Zn increased it by 8%. Mg is inherently basic and leads to a decrease in the strength of strong acidic sites. According to Karnjanakom et al., increased acidity in Zn-doped alumina is due to the substitution of

proton sites on the Al_2O_3 framework with the doping Zn species [37]. This substitution results in the regeneration of new proton sites on the support.

Figure 8. NH_3 -TPD profiles of Al_2O_3 supports and Pt/ Al_2O_3 catalysts.

Table 4. The acidity of supports and catalysts, determined by NH_3 -TPD.

Catalyst/Support	Temperature, °C		Total Acidity, mmol $\text{NH}_3/\text{g}_{\text{cat}}$	Peak Fraction	
	A	B		A	B
Al_2O_3	251	562	0.63	0.45	0.55
Mg- Al_2O_3	214	597	0.40	0.43	0.57
Zn- Al_2O_3	252	659	0.68	0.44	0.56
Pt/ Al_2O_3	236	566	0.48	0.52	0.48
Pt/Mg- Al_2O_3	202	565	0.41	0.56	0.44
Pt/Zn- Al_2O_3	250	575	0.49	0.60	0.40

A = first peak, B = second peak.

2.2.5. Transmission Electron Microscopy (TEM)

TEM images revealed the presence of Pt nanoparticles, as indicated by dark dispersed spherical particles, see Figure 9a–c. The measured d-spacing between the lattice fringes of the Pt/ Al_2O_3 particles was 2.07 Å and 2.4 Å. These d-spacing values correspond to the (200) and (111) family of planes, respectively. Furthermore, we obtained a d-spacing of 2.4 Å for Pt/Mg- Al_2O_3 catalyst. Miyazawa et al. measured a d-spacing of 2.3 Å, corresponding to the (111) plane [38]. For the Pt/Zn- Al_2O_3 catalyst, we obtained the d-spacing values 2.11 and 2.12 Å. These d-spacing values correspond to the d-spacing reported by the Joint Committee on Powder Diffraction Standards (JCPDS) files for face-centred cubic Pt. Table 5 summarises the measured d-values from fast Fourier transform (FFT) analysis, the family

of planes, which correspond to these spacings, and the error for the values reported in the literature.

(a)

(b)

Figure 9. Cont.

Figure 9. (a). TEM images, nanoparticles' size distribution histograms and FFT images of the Pt/Al₂O₃ catalyst. (b). TEM images, nanoparticles' size distribution histograms and FFT images of the Pt/Mg-Al₂O₃ catalyst. (c). TEM images, nanoparticles' size distribution histograms and FFT images of the Pt/Zn-Al₂O₃ catalyst.

Table 5. d-Spacing values from fast Fourier transform (FFT) measurements and Joint Committee on Powder Diffraction Standards (JCPDS).

hkl	Measured d-Value, Å	JCPDS d-Value, Å	Error, %
111	2.12	2.26	6
200	2.11	1.96	8
	2.07		5.6

The particle size diameter was obtained by measuring about 300 particles for each catalyst and fitting the plotted histograms using a log-normal distribution curve. The parameters of log-normal distribution (μ -lognormal mean and σ -lognormal standard deviation obtained after fitting the 300 particles) are used to calculate the actual mean (m) and mode (mo) of each catalyst using the equations below. The results are shown in Table 6.

$$[m = \exp(\mu + \sigma^2/2)] \quad (1)$$

$$[mo = \exp(\mu - \sigma^2)] \quad (2)$$

The obtained mean particle size is in the range from 1.54 to 1.72 nm for fresh catalysts, and from 2.14 to 2.80 nm for catalysts which sustained 22 h of dehydrogenation, see Figure 10 and Table 6. However, Pt particles were not observed for the Pt/Zn-Al₂O₃ sample and it could be that Zn affects nucleation and growth of particles, as reported by Belskaya [10]. The slight increase in particle size after 22 h of dehydrogenation reaction is negligible and cannot be linked to Pt sintering since it occurs at temperatures above 300 °C. The discrepancy in the particle size obtained from CO chemisorption and TEM have been reported elsewhere [2,39].

Table 6. Log-normal distribution parameters for mean and mode calculations of Pt nanoparticles obtained by transmission electron microscopy (TEM) before and after 22 h dehydrogenation reaction.

Catalyst	μ	σ	Mean	Mode
Before reaction				
Pt/Al ₂ O ₃	0.50	0.30	1.72	1.51
Pt/Mg-Al ₂ O ₃	0.52	0.18	1.70	1.62
Pt/Zn-Al ₂ O ₃	0.41	0.21	1.54	1.44
After 22 h dehydrogenation				
Pt/Al ₂ O ₃	1.00	0.24	2.80	2.57
Pt/Mg-Al ₂ O ₃	0.73	0.25	2.14	1.93
Pt/Zn-Al ₂ O ₃	-	-	-	-

Figure 10. Platinum nanoparticles' size distribution before and after dehydrogenation, experiments carried out at 300 °C for 22 h using a fixed bed reactor.

2.2.6. X-ray Diffraction (XRD)

Broad XRD peaks of pure alumina were detected at 32.5°, 37.0°, 38.9°, 45.0° and 67.5°. There was no difference between doped, undoped or Pt-loaded catalysts. This is because the Pt, Mg and Zn particles are small, and highly dispersed in the bulk alumina phase, and as such, they were undetectable by XRD. The positions at which the Pt peaks should

be observed are shown as vertical lines in Figure 11. The Pt loading was too low to be detected by XRD. For the Mg- and Zn-doped catalysts, there was no clear evidence of the existence of Mg and Zn oxides or aluminates (MgAl_2O_4 / ZnAl_2O_4) because their main peaks overlapped with those of alumina [8,40,41].

2.2.7. Characterisation of the Liquid Carrier Molecules

Here, we determined whether the by-products formed as a result of thermal cracking or by the nature of the support material or Pt catalyst. First, H18-DBT was heated without any catalyst or support material for 1.5 h at 300 °C. Second, in separate experiments, each support material (Al_2O_3 , Mg- Al_2O_3 and Zn- Al_2O_3) was added to fresh H18-DBT and treated under the same conditions as mentioned above. Pt/ Al_2O_3 catalyst was added at a later stage. The results did not indicate the presence of any by-products in the low and high boiler window of the spectrum when H18-DBT and all the supports were used (see Figure 12). However, by-products appeared when the catalyst was used. These by-products can be seen in Figure 12 as peaks in the low and high boiler region of the Pt/Mg- Al_2O_3 catalysts. This suggests that the operating conditions and support materials alone do not contribute to the formation of by-products, but the catalyst does. The aromatic molecules (H0-DBT) produced during dehydrogenation are susceptible to the acid sites of the support, which provides the cracking function. Hence, by-products were not seen in test of blank supports.

Figure 11. X-ray diffraction (XRD) patterns of catalysts and alumina supports.

Figure 12. The chromatograms of H18-DBT heated at 300 °C for 90 min with and without support, and a representative chromatogram and mass spectrometry (MS) spectra showing low boiling point by-products of Pt/Mg-Al₂O₃ catalyst. National Institute of Standards and Technology (NIST) 17 mass spectral library was used to identify the compounds.

3. Experimental

3.1. Materials

Dibenzyltoluene was purchased from Sasol (Marl, Germany) under the trade name Marlotherm-SH and further hydrogenated, using a nickel-based catalyst in a packed fixed bed reactor system, to obtain H18-DBT with a degree of hydrogenation (doh) of 99%. The spherically shaped catalyst support pellets (Al₂O₃, Mg-Al₂O₃, Zn-Al₂O₃) of diameter in the range of 1–3 mm were supplied by Sasol, Johannesburg, South Africa. The Mg-Al₂O₃ and Zn-Al₂O₃ were prepared by modification of parent unmodified γ -Al₂O₃ used in this study. Hexachloroplatinic acid hydrate (38% Pt basis) was purchased from Sigma Aldrich (Schnelldorf, Germany). The following gases were supplied by Afrox, Johannesburg, South Africa: H₂ (99.999%), N₂ (99.999%), He (99.999%), Ar (99.999%), CO/He (10%), NH₃/He (10%) and H₂/Ar (10% H₂). These gases were mainly used to supply the furnace setup and chemisorption equipment for catalyst processing and characterisation, respectively.

3.2. Catalyst Preparation

Chloroplatinic acid solution (0.025 M) was prepared by adding hexachloroplatinic acid hydrate (powder form) to deionised water. The solution was added to each alumina support to produce 0.5 wt.% Pt loading. A Büchi Rotavapor® R300 was used to evaporate water from pellets. The heating bath was set at 50 °C while the evaporating flask was under 46 mbar vacuum pressure and rotating at a speed of 40 rpm. An oven (Espec SU-221) was set at 120 °C to dry the pellets for a period of 4 h. Thereafter, pellets were calcined at 350 °C (ramp rate = 5 °C/min) in a stream of air (150 mL/min) for 5 h, using a furnace from Carbolite, UK. The calcined catalysts were reduced in a stream of 10% H₂/Ar (50 mL/min) over periods of 4 h at 350, 400 and 450 °C for Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃, respectively.

3.3. Catalyst Characterisation

3.3.1. Catalyst

The catalyst loading was confirmed by inductively coupled plasma–optical emission spectrometry (ICP-OES), using an Agilent 5110 ICP-OES instrument and the ICP Expert software. Catalysts were crushed and leached for 24 h, using a mixture of H₂O₂ and HCl (ratio 1:10) at 60 °C. The leachate was then analysed for the presence of Pt, Mg and Zn.

An ammonia temperature-programmed desorption (NH₃-TPD) experiment was performed to measure the acidity of the support and catalyst samples using an Auto-Chem II 2910 chemisorption analyser (Micromeritics, Norcross, GA, USA). Samples of 0.1 g of each catalyst were loaded in a U-type quartz sample tube. The analysis gas used was 10% NH₃/He. First, samples were pre-treated at 500 °C for 1 h under a He stream (30 mL/min). This was followed by saturation with NH₃ at 120 °C. A thermal conductivity detector provided quantitative measurements of NH₃ desorption in the temperature range of 100–900 °C, and a ramp rate of 10 °C/min.

Scanning electron microscopy (SEM) imaging was carried out using a FEI Quanta 250 field emission gun scanning electron microscope (ThermoFisher Scientific, Waltham, MA, USA), operating at an accelerating voltage of 15 kV. Energy-dispersive X-ray spectroscopy (EDS) line analysis was carried out using the Oxford Inca software. Line point samples were taken at an equidistance of 40 µm. All samples were coated with carbon using a magnetron sputtering, to allow conduction between the sample and a beam of electrons from the SEM-EDS instrumentation. The samples were then embedded in resin (conditions: 121 °C, 290 bar, 20 min), using a PR-10 Mounting Press (Leco, MI, USA). After mounting, the samples were cut to expose the pellets' cross-sectional area, as indicated in Figure 13.

Figure 13. Exposed cross-sectional areas of catalysts, for scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) line analysis.

Powder X-ray diffraction (XRD) analysis was performed using a D8-Advance all-purpose X-ray diffractometer (Bruker, Karlsruhe, Germany), operated in a locked coupled mode, with Cu-K α radiation ($\lambda = 1.5406$ Å) at 40 kV tube voltage and 40 mA tube current. The measurements were within the range 2θ (0–90°) and a position-sensitive Lynx-Eye detector was used. Diffraction data were recorded at a speed of 0.5 s/step, which is equivalent to 92 s/step for a scintillation counter.

3.3.2. Analysis of LOHC Molecule

Analysis of the LOHC molecule was performed using gas chromatography coupled to a single quadrupole mass spectrometer system (GC-SQ-MS) (Scion, Goes, The Netherlands). The system was equipped with a CP-8400 autosampler, a GS-Tek GsBP-50 + MS column (length 30 m, internal diameter 0.25 mm, film thickness 0.25 μm) and a single quadrupole mass spectrometer. Helium of 99.999% purity was used as a carrier gas. To perform liquid analyses, samples of the reaction mixture were drawn from the reactor and diluted with hexane (1:100 wt./wt.), and 1 μL aliquots of each sample were injected, at a split ratio of 1:100.

3.4. Dehydrogenation Activity Tests

Dehydrogenation of H18-DBT was performed using a system comprising of a horizontally oriented plug flow reactor made of quartz glass, see Figure 14. Prior to dehydrogenation experiments, the system is purged with nitrogen to remove air. Hydrogen-rich molecule (H18-DBT, >99% doh) is pumped into the reactor using a peristaltic pump (Medorex TL/150). The reactor is divided into three zones: (i) pre-heating zone packed with inert particles, (ii) reaction zone packed catalyst pellets and (iii) cooling zone packed with inert particles. An electrical heating jacket with three heating zones was used to supply heat and a thermocouple with the corresponding measurement points was centred horizontally through the reactor. During dehydrogenation reaction, the spent LOHC molecule from the reactor is cooled before reaching the product tank. Furthermore, the spent LOHC required for analysis is sampled before the product tank. Hydrogen gas passes through a cooling condenser and a carbon filter prior flow measurement by a mass flow meter (EL-Flow F11B-500-AGD-22V, Bronkhorst; flow range 0.16 to 3.5 nL/min; accuracy $\pm 0.5\%$ Reading). This dehydrogenation system is controlled by Siemens PLC and for all experiments, a constant feed flow (1.3 mL/min) and reaction temperature (300 $^{\circ}\text{C}$) were used.

Figure 14. Process flow diagram of the fixed-bed reactor dehydrogenation unit.

The catalyst productivity (P), H_2 -yield, conversion (X) and selectivity (S) are calculated using the following equations:

$$P = m_{\text{H}_2} / m_{\text{Pt}} \cdot t \quad (3)$$

$$\text{H}_2\text{-yield} = [\text{V}_{\text{H}_2 \text{ released}} / \text{V}_{\text{H}_2 \text{ max}}] \times 100 \quad (4)$$

$$X_{\text{H18-DBT}} = [\text{mol}_{\text{H18-DBT (in)}} - \text{mol}_{\text{H18-DBT (out)}}] / (\text{mol}_{\text{H18-DBT (in)}}) \times 100 \quad (5)$$

$$S_{\text{H0-DBT}} = [(\text{mol}_{\text{H0-DBT}}) / (\text{mol}_{\text{H0-DBT}} + \text{mol}_{\text{H12-DBT}} + \text{mol}_{\text{H6-DBT}} + \text{mol}_{\text{by-products}})] \times 100 \quad (6)$$

where m_{H_2} is the mass of released hydrogen, m_{Pt} is mass of platinum, t is time in minutes, $V_{\text{H}_2 \text{ released}}$ is the volume of hydrogen released and $V_{\text{H}_2 \text{ max}}$ is the theoretical maximum amount of hydrogen stored in H18-DBT.

4. Conclusions

The addition of Mg and Zn dopants strengthened metal–support interaction, decreased Pt particle size and dispersion and changed the acidity of supports. Pt/Mg-Al₂O₃ showed improved catalytic performance when compared to Pt/Zn-Al₂O₃ and Pt/Al₂O₃ catalysts, and the higher the reaction activity, the higher the amounts of by-products. This is because the higher the catalytic activity, the more aromatic molecules are produced, and these aromatic molecules are susceptible to the acid sites of the support, which provides the cracking function. Furthermore, the formation of by-products could be facilitated by the hydrogenolytic effect of Pt/Mg-Al₂O₃. The improved activity of Pt/Mg-Al₂O₃ can be attributed to the fact that Mg improves reduction of Pt-oxide and this has led to higher metallic Pt concentration (active sites) on Pt/Mg-Al₂O₃ than that on Pt/Al₂O₃ and Pt/Zn-Al₂O₃. The Al₂O₃ grain size could be densified by Mg addition, and the larger the grain size, the larger the pores. This has an effect on minimizing the pore diffusion limitation and increasing the catalytic activity.

Author Contributions: Conceptualisation, J.V. and P.v.H.; Data curation, R.G.; Formal analysis, P.M.; Funding acquisition, J.V., P.v.H. and D.B.; Resources, I.S.; Supervision, D.B.; Writing—original draft, R.G.; Writing—review and editing, P.M. All authors have read and agreed to the published version of the manuscript.

Funding: Financial support from Sasol and Department of Science and Innovation (DSI) through KP5 Program, as well as NRF (grant no. 104687 and 119004) is gratefully acknowledged.

Data Availability Statement: The data supporting the findings of this study are available within the article.

Acknowledgments: We express special gratitude to Lia Van Zyl of Sasol South Africa for providing necessary logistics.

Conflicts of Interest: There are no conflict of interest to declare.

References

1. Modisha, P.M.; Ouma, C.N.; Garidzirai, R.; Wasserscheid, P.; Bessarabov, D. The prospect of hydrogen storage using liquid organic hydrogen carriers. *Energy Fuels* **2019**, *33*, 2778–2796. [\[CrossRef\]](#)
2. Modisha, P.; Gqogqa, P.; Garidzirai, R.; Ouma, C.N.M.; Bessarabov, D. Evaluation of catalyst activity for release of hydrogen from liquid organic hydrogen carriers. *Int. J. Hydrogen Energy* **2019**, *44*, 21926–21935. [\[CrossRef\]](#)
3. Bessarabov, D.; Human, G.; Kruger, A.J.; Chiuta, S.; Modisha, P.M.; Du Preez, S.P.; Oelofse, S.P.; Vincent, I.; Van Der Merwe, J.; Langmi, H.W.; et al. South African hydrogen infrastructure (HySA infrastructure) for fuel cells and energy storage: Overview of a projects portfolio. *Int. J. Hydrogen Energy* **2017**, *42*, 13568–13588. [\[CrossRef\]](#)
4. Ouma, C.N.; Modisha, P.; Bessarabov, D. Insight into the adsorption of a liquid organic hydrogen carrier, perhydro-*i*-dibenzyltoluene (*i* = m, o, p), on Pt, Pd and PtPd planar surfaces. *RSC Adv.* **2018**, *8*, 31895–31904. [\[CrossRef\]](#)
5. Amende, M.; Kaftan, A.; Bachmann, P.; Brehmer, R.; Preuster, P.; Koch, M.; Wasserscheid, P.; Libuda, J. Regeneration of LOHC dehydrogenation catalysts: In-situ IR spectroscopy on single crystals, model catalysts, and real catalysts from UHV to near ambient pressure. *Appl. Surf. Sci.* **2016**, *360*, 671–683. [\[CrossRef\]](#)
6. Ballarini, A.; Basile, F.; Benito, P.; Bersani, I.; Fornasari, G.; de Miguel, S.; Maina, S.C.P.; Vilella, J.; Vaccari, A.; Scelza, O.A. Platinum supported on alkaline and alkaline earth metal-doped alumina as catalysts for dry reforming and partial oxidation of methane. *Appl. Catal. A Gen.* **2012**, *433–434*, 1–11. [\[CrossRef\]](#)
7. Yu, C.; Xu, H.; Ge, Q.; Li, W. Properties of the metallic phase of zinc-doped platinum catalysts for propane dehydrogenation. *J. Mol. Catal. A Chem.* **2007**, *266*, 80–87. [\[CrossRef\]](#)
8. Buitrago-Sierra, R.; Ruiz-Martínez, J.; Serrano-Ruiz, J.C.; Rodríguez-Reinoso, F.; Sepúlveda-Escribano, A. Ethanol steam reforming on Ni/Al₂O₃ catalysts: Effect of addition of Zn and Pt. *J. Colloid Interface Sci.* **2012**, *383*, 148–154. [\[CrossRef\]](#)

9. Zhang, Y.; Zhou, Y.; Huang Li Zhou, S.; Sheng, X.; Wang, Q.; Zhang, C. Structure and catalytic properties of the Zn-modified ZSM-5 supported platinum catalyst for propane dehydrogenation. *Chem. Eng. J.* **2015**, *270*, 352–361. [CrossRef]
10. Belskaya, O.B.; Stepanova, L.N.; Gulyaeva, T.I.; Erenburg, S.B.; Trubina, S.V.; Kvashnina, K.; Nizovskii, A.I.; Kalinkin, A.V.; Zaikovskii, V.I.; Bukhtiyarov, V.I.; et al. Zinc influence on the formation and properties of Pt/Mg(Zn)AlO_x catalysts synthesised from layered hydroxides. *J. Catal.* **2016**, *341*, 13–23. [CrossRef]
11. Berry, A.K.; Harmer, M.P. Effect of MgO solute on microstructure development in Al₂O₃. *J. Am. Ceram. Soc.* **1986**, *69*, 143–149. [CrossRef]
12. Clavenna, L.R.; Davis, S.M.; Fiato, R.A.; Say, G.R. Structurally Modified Alumina Supports, and Heat Transfer Solids for High Temperature Fluidized Bed Reactions. U.S. Patent 5,395,406, 7 March 1995. Available online: <https://patents.google.com/patent/US5395406A/en> (accessed on 17 January 2021).
13. Zhou, Y.; Davis, S.M. Dehydrogenation Catalysts and Process for Preparing the Catalysts. U.S. Patent 5,219,816, 15 June 1993. Available online: <https://patents.google.com/patent/US5219816A/en> (accessed on 17 January 2021).
14. Biniwale, R.B.; Pande, J.V.; Shukla, A. Process for the Storage Delivery of Hydrogen Using Catalyst. U.S. Patent 9,005,571, 14 April 2015. Available online: <https://patents.google.com/patent/US9005571B2/en> (accessed on 17 January 2021).
15. Martins, A.R.; Santos, L.; Patricio, C.; Javier, R.; Grau, M.; do Carmo Rangel, M. Hydrogen production on alumina-supported platinum catalysts. *J. Mol. Catal. A Chem.* **2017**, *429*, 1–9. [CrossRef]
16. Escobar, J.; Barrera, M.C.; Santes, V.; Terrazas, J.E. Naphthalene hydrogenation over Mg-doped Pt/Al₂O₃. *Catal. Today* **2017**, *296*, 197–204. [CrossRef]
17. Kumar, M.; Aberuagba, F.; Gupta, J.K.; Rawat, K.S.; Sharma, L.D.; Dhar, G.M. Temperature-programmed reduction and acidic properties of molybdenum supported on MgO-Al₂O₃ and their correlation with catalytic activity. *J. Mol. Catal. A Chem.* **2004**, *213*, 217–223. [CrossRef]
18. Zhang, Y.; Zhou, Y.; Wan, L.; Xue, M.; Duan, Y.; Liu, X. Effect of magnesium addition on catalytic performance of PtSnK/γ-Al₂O₃ catalyst for iso-butane dehydrogenation. *Fuel Process. Technol.* **2011**, *92*, 1632–1638. [CrossRef]
19. Arnby, K.; Törnroona, A.; Skoglundh, M. Influence of ammonia on CO and methanol oxidation over Pt/γ-Al₂O₃ catalysts modified by Mg. *Appl. Catal. B Environ.* **2004**, *49*, 51–59. [CrossRef]
20. Zhan, Y.Y.; Liang, K.A.; Zhou, Y.C.; Cai, G.H.; Chen, C.Q.; Jiang, L.L. Pd/Al₂O₃ catalysts modified with Mg for catalytic combustion of methane: Effect of Mg/Al mole ratios on the supports and active PdO_x formation. *J. Fuel Chem. Technol.* **2019**, *47*, 1235–1244. [CrossRef]
21. Auer, F.; Blaumeiser, D.; Bauer, T.; Bösmann, A.; Szesni, N.; Libuda, J.; Wasserscheid, P. Boosting the activity of hydrogen release from liquid organic hydrogen carrier systems by sulfur-additives to Pt on alumina catalysts. *Catal. Sci. Technol.* **2019**, *9*, 3537–3547. [CrossRef]
22. Bai, L.; Zhou, Y.; Zhang, Y.; Liu, H.; Sheng, X. Effect of magnesium addition to PtSnNa/ZSM-5 on the catalytic properties in the dehydrogenation of propane. *Ind. Eng. Chem. Res.* **2009**, *48*, 9885–9891. [CrossRef]
23. Shi, J.; Zhou, Y.; Zhang, Y.; Zhou, S.; Zhang, Z.; Kong, J.; Guo, M. Synthesis of magnesium-modified mesoporous Al₂O₃ with enhanced catalytic performance for propane dehydrogenation. *J. Mater. Sci.* **2014**, *49*, 5772–5781. [CrossRef]
24. Xue, M.W.; Zhou, Y.M.; Zhang, Y.W.; Huang, L.; Duan, Y.Z. Effects of Mg addition on catalytic performance of PtNa/Sn-ZSM-5 in propane dehydrogenation. *Acta Phys. Chim. Sin.* **2012**, *28*, 928–934.
25. Posner, G.H. Organic Reactions at Alumina Surfaces. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 487–496. [CrossRef]
26. Modisha, P.M.; Jordaan, J.H.; Bösmann, A.; Wasserscheid, P.; Bessarabov, D. Analysis of reaction mixtures of perhydrodibenzyltoluene using two-dimensional gas chromatography and single quadrupole gas chromatography. *Int. J. Hydrogen Energy* **2018**, *43*, 5620–5636. [CrossRef]
27. Bocanegra, S.A.; Guerrero-Ruiz, A.; de Miguel, S.R.; Scelza, O.A. Performance of PtSn catalysts supported on MA₂O₄ (M: Mg or Zn) in n-butane dehydrogenation: Characterisation of the metallic phase. *Appl. Catal. A Gen.* **2004**, *277*, 11–22. [CrossRef]
28. Park, J.E.; Kim, B.B.; Park, E.D. Propane combustion over Pt/Al₂O₃ catalysts with different crystalline structures of alumina. *Korean J. Chem. Eng.* **2015**, *32*, 2212–2219. [CrossRef]
29. Aguilar-Ríos, G.; Valenzuela, M.; Salas, P.; Armendáriz, H.; Bosch, P.; Del Toro, G.; Silva, R.; Bertín, V.; Castillo, S.; Ramírez-Solís, A.; et al. Hydrogen interactions and catalytic properties of platinum–tin supported on zinc aluminate. *Appl. Catal. A Gen.* **1995**, *127*, 65–75. [CrossRef]
30. Bensaddik, A.; Mouaddib, N.; Pitchon, V.; Garin, F.; Maire, G.; Krawczyk, M. Promoting effect of zinc in DeNO_x reaction over Pt/Al₂O₃. Catalysis and Automotive Pollution Control IV. *Stud. Surf. Sci. Catal.* **1998**, *116*, 265–274. [CrossRef]
31. Consonni, M.; Jokic, D.; Murzin, Y.D.; Touroude, R. High performances of Pt/ZnO catalysts in selective hydrogenation of crotonaldehyde. *J. Catal.* **1999**, *188*, 165–175. [CrossRef]
32. Berteau, P.; Delmon, B. Modified aluminas: Relationship between activity in 1-butanol dehydration and acidity measured by NH₃-TPD. *Catal. Today* **1989**, *5*, 121–137. [CrossRef]
33. Gutiérrez-Alejandra, A.; González-Cruza, M.; Trombetta, M.; Buscab, G.; Ramírez, J. Characterisation of alumina-titania mixed oxide supports: Part II: Al₂O₃-based supports. *Microporous Mesoporous Mater.* **1998**, *23*, 265–275. [CrossRef]
34. Shi, Y.; Li, X.; Rong, X.; Gu, B.; Wei, H.; Sun, C. Influence of support on catalytic properties of Pt-Sn-K/θ-Al₂O₃ for propane dehydrogenation. *RSC Adv.* **2017**, *7*, 19841–19848. [CrossRef]

-
35. Stanislaus, A.; Absi-Halabi, M.; Al-Doloma, K. Effect of phosphorous on the acidity of γ -alumina and on the thermal stability of γ -alumina supported nickel-molybdenum hydrotreating catalysts. *Appl. Catal. A Gen.* **1988**, *39*, 239–253. [[CrossRef](#)]
 36. Laniecki, M.; Małeck-Grycz, M.; Domka, F. Water–gas shift reaction over sulfided molybdenum catalysts: I. Alumina, titania and zirconia-supported catalysts. *Appl. Catal. A Gen.* **2000**, *196*, 293–303. [[CrossRef](#)]
 37. Karnjanakom, S.; Bayu, A.; Hao, X.; Kongparakul, S.; Samart, C.; Abudula, A.; Guan, G. Selectively catalytic upgrading of bio-oil to aromatic hydrocarbons over Zn, Ce or Ni-doped mesoporous rod-like alumina catalysts. *J. Mol. Catal. A Chem.* **2016**, *421*, 235–244. [[CrossRef](#)]
 38. Miyazawa, K.; Yoshitake, M.; Tanaka, Y. HRTEM analyses of the platinum nano-particles prepared on graphite particles using coaxial arc plasma deposition. *J. Nanopart. Res.* **2017**, *19*, 191–199. [[CrossRef](#)]
 39. Kirilin, A.V.; Hasse, B.; Tokarev, A.V.; Kustov, L.M.; Baeva, G.N.; Bragina, G.O.; Stakheev, A.Y.; Rautio, A.R.; Salmi, T.; Etzold, B.J.; et al. Aqueous-phase reforming of xylitol over Pt/C and Pt/TiC-CDC catalysts: Catalyst characterization and catalytic performance. *Catal. Sci. Technol.* **2014**, *4*, 387–401. [[CrossRef](#)]
 40. Zhang, H.; Wan, H.; Zhao, Y.; Wang, W. Effect of chlorine elimination from Pt-Sn catalyst on the behavior of hydrocarbon reconstruction in propane dehydrogenation. *Catal. Today* **2019**, *330*, 85–91. [[CrossRef](#)]
 41. Bai, Q.; Li, D.; He, L.; Xiao, H.; Sui, N.; Liu, M. Solvent-free selective hydrogenation of o-chloronitrobenzene to o-chloroaniline over alumina supported Pt nano-particles. *Prog. Nat. Sci. Mater. Int.* **2015**, *25*, 179–184. [[CrossRef](#)]