

Article

Assessment of Reaction Kinetics for the Dehydrogenation of Perhydro-Dibenzyltoluene Using Mg- and Zn-Modified Pt/Al₂O₃ Catalysts

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Abstract: The catalysts utilized for the dehydrogenation of dibenzyltoluene-based liquid organic hydrogen carriers (LOHCs) remain crucial. The state-of-the-art catalyst for dehydrogenation of dibenzyltoluene-based LOHC still suffers from deactivation and by-product formation. This is crucial in terms of the efficiency of the industrial dehydrogenation plant for hydrogen production, cyclability as well as the cost of replacing the catalyst. The development of catalysts with optimum performance, minimum deactivation and low by-product formation is required to attain the full benefits of the LOHC technology. Therefore, in this study, the effect of Mg and Zn modification on Pt/Al₂O₃ catalyst is investigated for the catalytic dehydrogenation of perhydro-dibenzyltoluene (H18-DBT). In addition, an assessment of reaction kinetics is also conducted. High dehydrogenation performance was obtained for Mg-doped Pt/Al₂O₃ using a batch reactor at 300 °C and 6 h reaction time. In this case, the degree of dehydrogenation (dod), productivity and conversion obtained are 100%, 1.84 gH₂/gPt/min and 99.9%, respectively. Moreover, the Mg-doped catalyst has resulted in a high turnover frequency (TOF) of 586 min^{−1} compared to the Zn-doped catalyst (269 min^{−1}) and the undoped catalyst (202 min^{−1}) at the reaction temperature of 300 °C. The amount of by-products increased with an increase in the catalytic activity, with the Pt/Mg-Al₂O₃ catalyst possessing the highest amount of by-products. The dehydrogenation of H18-DBT followed first-order reaction kinetics. In addition, the activation energy obtained using the Arrhenius model is 102, 130 and 151 kJ/mol for Pt/Al₂O₃, Pt/Zn-Al₂O₃ and Pt/Mg-Al₂O₃, respectively. Although the Mg-doped Pt/Al₂O₃ shows high activation energy, the higher performance of the catalyst suggests that mass transfer limitations have no major effect on the dehydrogenation reaction under the conditions used.

Keywords: liquid organic hydrogen carriers; perhydro-dibenzyltoluene; dehydrogenation; reaction kinetics; Pt/Al₂O₃ catalyst



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1. Introduction

Hydrogen is one of the most pursued alternative energy carriers due to its high gravimetric energy density (33 kWh/kg), which is higher than most conventional fuels [1]. It is also a clean energy carrier and a feedstock that has the potential to decarbonize various fossil-based sectors, such as petrochemicals, chemicals, glass, cement, steel, etc. Specifically, Hydrogen has a low density (0.0813 g/L at STP), resulting in low energy per volume; hence, efficient storage methods are needed [2]. Several hydrogen storage technologies, such as high-pressure gas cylinders, liquefied hydrogen, ammonia, metal hydrides and liquid organic hydrogen carriers (LOHCs), have been explored to mitigate the storage challenges [3]. Amongst the different storage mediums, LOHC technology offers numerous advantages over conventional hydrogen storage technologies. This is because hydrogen can be stored on a large scale for long periods of time without losses when using LOHC technology, whilst hydrogen storage in cylinders or as liquified hydrogen has potential losses. Dibenzyltoluene (H0-DBT) has been identified as one of the most promising LOHC

molecules for hydrogen storage because of its attractive hydrogen storage properties [4]. Hydrogen is stored by the catalytic hydrogenation of H0-DBT to produce the hydrogen-rich molecule known as perhydrodibenzyltoluene (H18-DBT). Since this is a reversible process, hydrogen is released by catalytic dehydrogenation of H18-DBT to produce dibenzyltoluene as a hydrogen lean molecule. The H0-DBT/H18-DBT LOHC system is non-flammable, not classified as dangerous goods, remains liquid at sub-zero temperatures and has a high storage capacity (6.2 wt %, 57 kg-H₂/m³-H18-DBT) and boiling point (380 °C) [4,5]. Other attractive properties of this system include its compatibility with existing infrastructure for fuel, industrial-scale production and cost-effectiveness (3–4 €/kg) [4,5]. Platinum has been the most widely used catalyst for the dehydrogenation of H18-DBT in the production of hydrogen [6–11]. However, Pt-based catalysts (e.g., Pt/Al₂O₃) are prone to deactivation during the dehydrogenation process, which suggests a loss in the activity of the active sites [12,13]. Over time, this will lead to a reduction in the efficiency of the dehydrogenation system as well as the cost implications associated with frequent catalyst replacement. Various efforts have been employed to improve performance and reduce by-products. This includes, but is not limited to, surface pre-treatment of catalysts [6], support modifications [13–15] and utilization of different methods of catalyst synthesis [16].

The EU-supported SHERLOHCK consortium has set criteria which dehydrogenation catalysts should meet [17]. This includes a productivity of >3 gH₂/g_{catalyst}/min and low energy demand (<6 kWh/kg-H₂) while maintaining high conversion (>90%) and selectivity of >99.8%. The initial catalyst performance screening tests for dehydrogenation of H18-DBT were first conducted by Brückner et al. [3]. The high catalytic activity was reported for Pt/C with a hydrogen yield of 71% after 3.5 h at 270 °C. This was followed by Pt/Al₂O₃, Pd/C, Pt/SiO₂ and Pd/Al₂O₃, with a degree of dehydrogenation (dod) of 51%, 16%, 10% and 8%, respectively. It can be deduced from the screening results that SiO₂ support and Pd-based catalysts are not suitable for H18-DBT dehydrogenation. The work of Modisha et al. [12] also confirmed that Pt has high catalytic performance for dehydrogenation of H18-DBT compared to Pd and Pt–Pd supported on Al₂O₃. To date, several hydrogenation and dehydrogenation cycles have been attempted and the presence of by-products has been observed in each cycle. The liquid-based by-products (e.g., benzyltoluene and benzylmethylfluorene) are also LOHCs that could subsequently affect the properties (e.g., viscosity, boiling point, etc.) of the parent molecules [18]. Gaseous by-products in the hydrogen effluent, such as CH₄, CO and CO₂, have been found to be due to the presence of impurities (water and oxygenates) in the LOHC [12,19,20].

The catalyst can be modified to improve its activity and stability and to reduce the formation of by-products. Recently, Shi et al. [6] modified the surface hydroxyl groups and oxygen vacancies of Al₂O₃ using H₂ and O₂ dielectric barrier discharge plasma. Both treatments led to decreased Pt size and improved Pt dispersion for Pt/Al₂O₃ (3 wt %). The hydrogen-treated catalyst showed improved catalytic performance because the modification increased surface hydroxyl groups. There are a few publications that report on the effect of modifiers/dopants on the dehydrogenation of H18-DBT. Auer et al. [14] investigated the effect of sulphur dopant on the dehydrogenation of H18-DBT using 0.3 wt % Pt/Al₂O₃. The appropriate sulphur loading (0.25 wt %) reduced the formation of by-products and improved the dod from 78% to >90%. Likewise, Chen et al. [15] modified 3 wt % Pt/Al₂O₃ and Pt/TiO₂ using 0.25 wt % sulphur. Doping with sulphur improved the activity of both catalysts; however, Pt/Al₂O₃ produced more by-products than Pt/TiO₂. Furthermore, a sulphur loading of 0.5 wt % on Pt/Al₂O₃ showed higher dod (95%) compared to undoped Pt/Al₂O₃ with a dod of 81%. Apart from sulphur, other dopants have been considered. For example, Seidel [21] studied dopants such as lithium, potassium and caesium in different ratios for modification of the Pt/Al₂O₃ catalyst. A dopant to Pt ratio of 5.7 was found to be the optimum, with the lithium dopant showing high dod (85%).

Although the abovementioned strategies have been beneficial, there is still a need to comprehend the reaction kinetics for the dehydrogenation of H18-DBT. Further catalyst development work will be beneficial for the optimization of reaction conditions and,

ultimately, the improvement of the reactor design. It is reported that the dehydrogenation of H18-DBT depends on the mass transport of the molecules, which involves the diffusion of reactants and products to and from the catalyst pores [10]. The kinetic models that have been developed for the dehydrogenation of H18-DBT are based on typical Pt/Al₂O₃ catalysts, but the effect of dopants on the kinetic parameters has not been fully explored. Peters et al. [22] developed a kinetic model for H18-DBT dehydrogenation using 5 wt % Pt/Al₂O₃ in a fixed bed reactor at temperatures from 290 to 350 °C. First-order reaction kinetics was obtained, with activation energy (*E_a*) and turnover frequency (TOF) of 117 kJ/mol and 120 s^{−1}, respectively. The Pt/Al₂O₃ catalyst was also used by Park et al. [23] for the dehydrogenation of H18-DBT at temperatures ranging from 250 to 320 °C using a continuous flow reactor. The reaction rate orders obtained were between 2.3 and 2.4, with an activation energy of 171 kJ/mol. Modisha et al. [18] obtained an activation energy of 201 kJ/mol using a batch reactor. A microchannel reactor indicated improved reaction kinetics compared with conventional reactors [8]. According to the literature, metal doping could lead to changes in the electronic, structural and chemical properties of the catalyst, which affects the catalyst's performance [14,15,24,25]. In this study, the effects of Mg and Zn dopants on the Pt/Al₂O₃ catalyst performance and reaction kinetics were investigated for the dehydrogenation of H18-DBT using a batch reactor.

2. Results and Discussion

This section addresses the results of the effect of reaction temperature and dopants on the catalytic dehydrogenation performance of H18-DBT and the dehydrogenation kinetics.

2.1. Evaluation of Catalytic Performance for Dehydrogenation of H18-DBT Using a Batch Reactor

The effect of the dehydrogenation reaction temperature on catalytic performance was evaluated using a batch reactor at temperatures in the range of 260–300 °C. The catalysts were subjected to four dehydrogenation cycles (runs) to determine the catalytic performance. The four dehydrogenation runs (run 1, run 2, run 3 and run 4) were also used to determine the stability of the catalysts. To determine the reaction kinetics for the dehydrogenation of H18-DBT, run 4 was used as it showed stability. Stability in this instance means the activity of catalysts was constant for at least two consecutive runs.

Figure 1 displays the effect of reaction temperature on hydrogen flow, productivity and the dod between 260 and 300 °C for the Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ catalysts. When the dehydrogenation reaction temperature was increased, there was an increase in hydrogen flow, productivity and dod. This is expected because an increase in temperature increases the rate of reaction, resulting in higher activity. A linear increase was observed for hydrogen flow and productivity in all runs. The activity of the catalysts decreased after the first run, yet some stability was observed between runs 3 and 4 (see also hydrogen flow and dod vs. time in Figure S1). This decrease is due to catalyst deactivation. In run 1, there was no apparent difference in hydrogen flow and productivity between 260 and 280 °C; however, at 290 and 300 °C, slight differences were observed. In runs 2–4 and at temperature ranges of 260–290 °C, the activity of all catalysts was similar, but the Mg-doped catalyst exhibited the highest activity at 300 °C. The fresh Pt/Mg-Al₂O₃ catalyst produced a 100% dod at 290 °C for run 1, while, at the same temperature, the Pt/Al₂O₃ and Pt/Zn-Al₂O₃ catalysts produced a dod of 78%. Pt/Zn-Al₂O₃ and Pt/Al₂O₃ did not provide full dehydrogenation at the studied temperatures. After the first run, Pt/Mg-Al₂O₃ still exhibited the highest dod of 73% compared with values of 60% and 50% observed for Pt/Zn-Al₂O₃ and Pt/Al₂O₃, respectively.

The unmodified Pt/Al₂O₃ used in this work showed a productivity of 1.62 gH₂/g_{Pt}/min, whereas literature work [14,15] reported a range of 0.6–1.2 gH₂/g_{Pt}/min. The Mg- and Zn-doped catalysts showed productivities of 1.84 and 1.68 gH₂/g_{Pt}/min, respectively. This is comparable with the values obtained by Auer et al. [14] and Chen et al. [15]. These authors found that doping the 0.3 wt % Pt/Al₂O₃ with sulphur resulted in productivities of 2 and 1.5 gH₂/g_{Pt}/min, respectively. An improved productivity of 2 gH₂/g_{Pt}/min was ob-

tained with low Pt loading (0.3 wt %) [14] compared to the productivity of 1.84 gH₂/g_{Pt}/min obtained in this study using 0.5 wt % Pt/Al₂O₃ (see Figure 2). This is because high Pt dispersion is achieved with low Pt loading, which results in improved catalytic activity [14,15]. Nonetheless, it is considered that the performances recorded in this study are comparable with literature work.

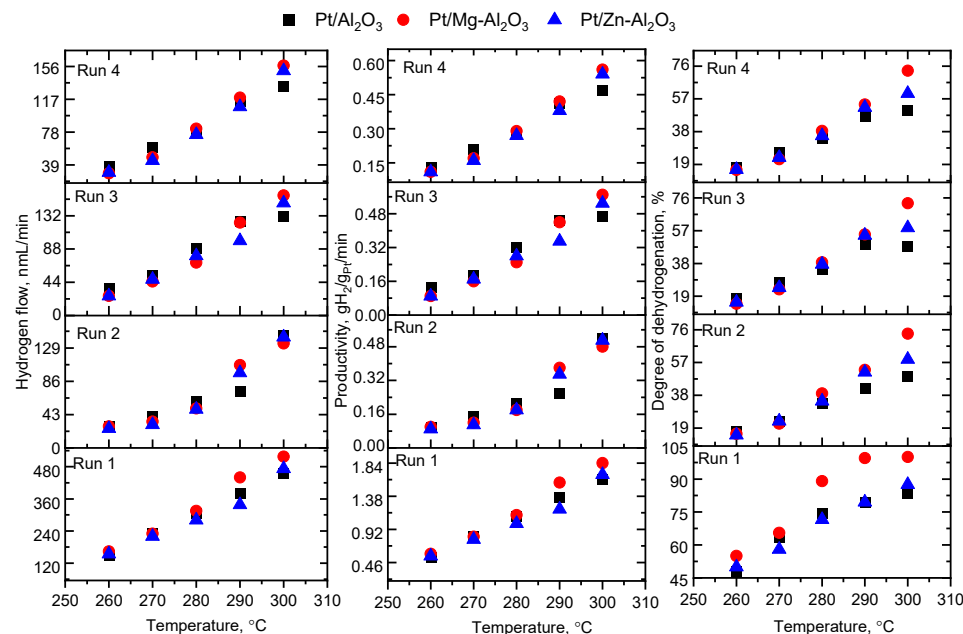


Figure 1. The effect of temperature on hydrogen flow, productivity and doh. Reaction parameters: H18-DBT degree of hydrogenation (doh), 99%; 0.5 wt % Pt/Al₂O₃; Pt to H18-DBT molar ratio ($n_{\text{Pt}}/n_{\text{LOHC}}$), 0.2 mol %; temperature, 260–300 °C; time, 90 min.

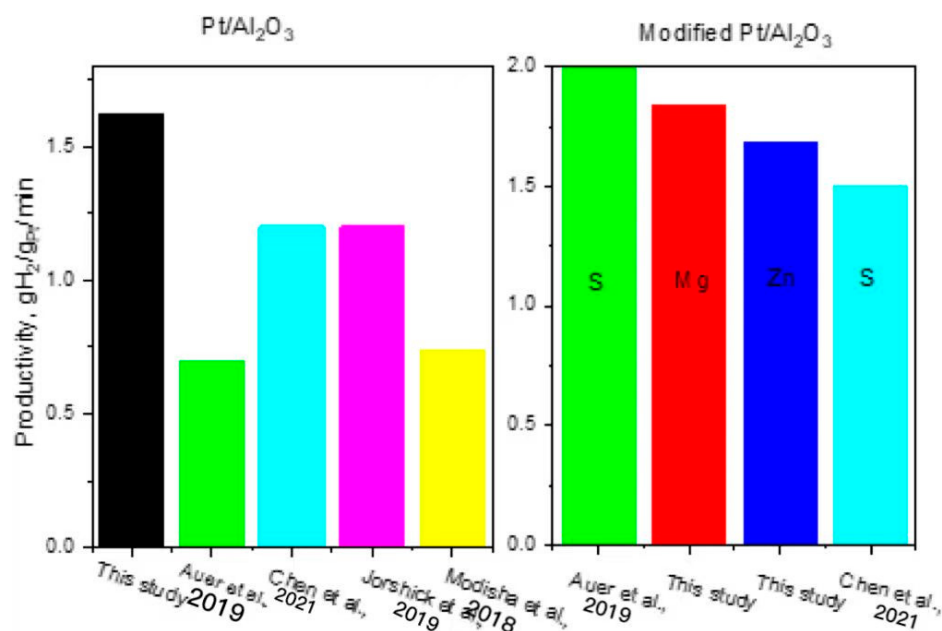


Figure 2. Comparison of productivity of doped and undoped Pt/Al₂O₃ catalysts used for H18-DBT dehydrogenation in a batch reactor: this study vs. literature [14,15,26,27].

In this study, Mg appears to be the best dopant for the dehydrogenation of H18-DBT. The improved performance of the Pt/Mg-Al₂O₃ catalyst could be due to the reduction in deactivation by the Mg dopant, as will be expanded upon in the discussion below. The

comparison of the productivity of the catalysts prepared in this work and the literature work is presented in Figure 2.

The effects of temperature and dopants on the conversion, selectivity and by-product formation were investigated by analyzing the LOHC samples using gas chromatography single quadrupole mass spectroscopy (GC-SQ-MS). During the dehydrogenation of H18-DBT, the intermediates H12-DBT and H6-DBT are formed and then also become dehydrogenated to produce H0-DBT. Therefore, the dehydrogenation of H18-DBT follows the following order: $\text{H18-DBT} \cdot 3\text{H}_2 \rightarrow \text{H12-DBT} \cdot 3\text{H}_2 \rightarrow \text{H6-DBT} \cdot 3\text{H}_2 \rightarrow \text{H0-DBT}$. Figure 3 shows the total ion chromatogram of the LOHC reaction mixture.

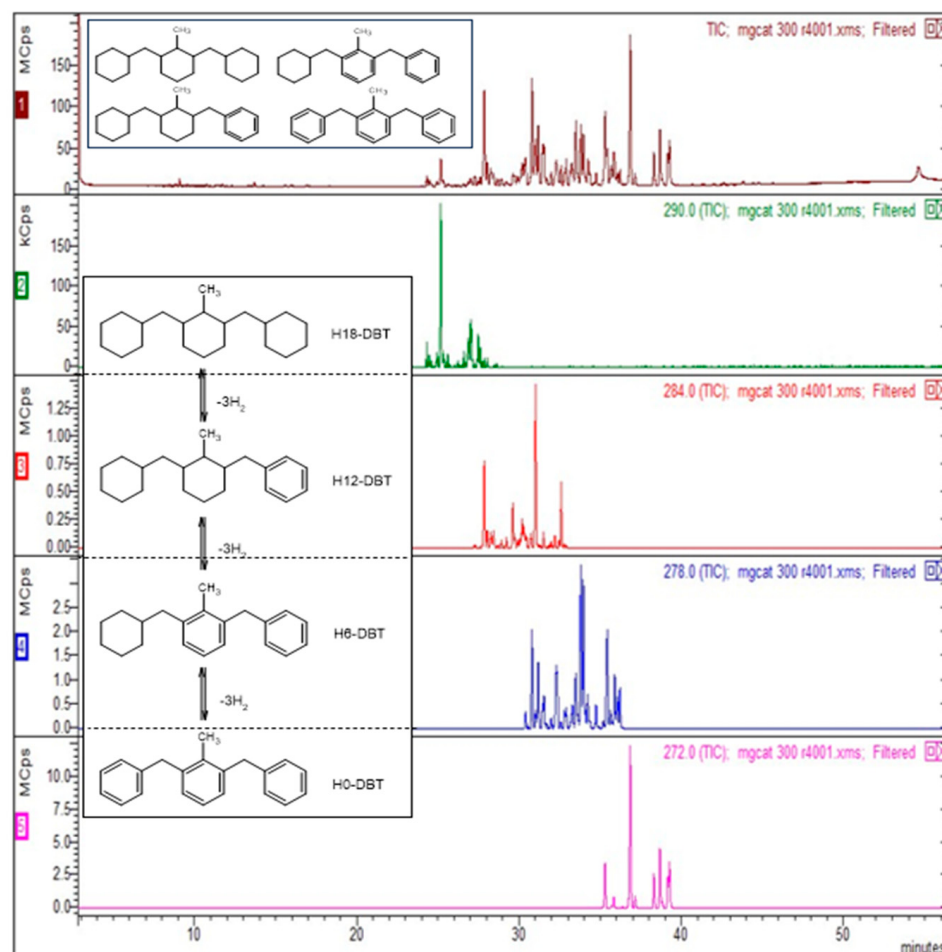


Figure 3. Total ion chromatogram of the LOHC reaction mixture obtained after 300 °C using Pt/Mg-Al₂O₃ catalyst. Insert: H18-DBT reaction pathway.

In the dehydrogenation of H18-DBT at 300 °C, fresh and used catalysts (from run 1 to run 4) showed conversions of >90% for Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ used in this study (Figure 4) (Figure 5). However, the H18-DBT conversion of the used catalyst was significantly low (~40% decrease) at temperatures from 260 °C to 270 °C. This phenomenon can be explained by the fact that the dehydrogenation of H18-DBT is endothermic and sensitive to temperature changes. Although the difference in conversion for all catalysts at the same temperature is less pronounced, the H0-DBT selectivity for the Pt/Mg-Al₂O₃ catalysts is remarkable. At the reaction temperature of 290 °C, the Pt/Mg-Al₂O₃, Pt/Al₂O₃ and Pt/Zn-Al₂O₃ catalysts showed H0-DBT selectivities of 87%, 72% and 77%, respectively. A comparable selectivity was obtained for all catalysts with an apparent difference at 300 °C. In run 4, Pt/Al₂O₃ showed the lowest selectivity (35%), while Pt/Zn-Al₂O₃ and Pt/Mg-Al₂O₃ showed selectivities of 49% and 62%, respectively, at 300 °C.

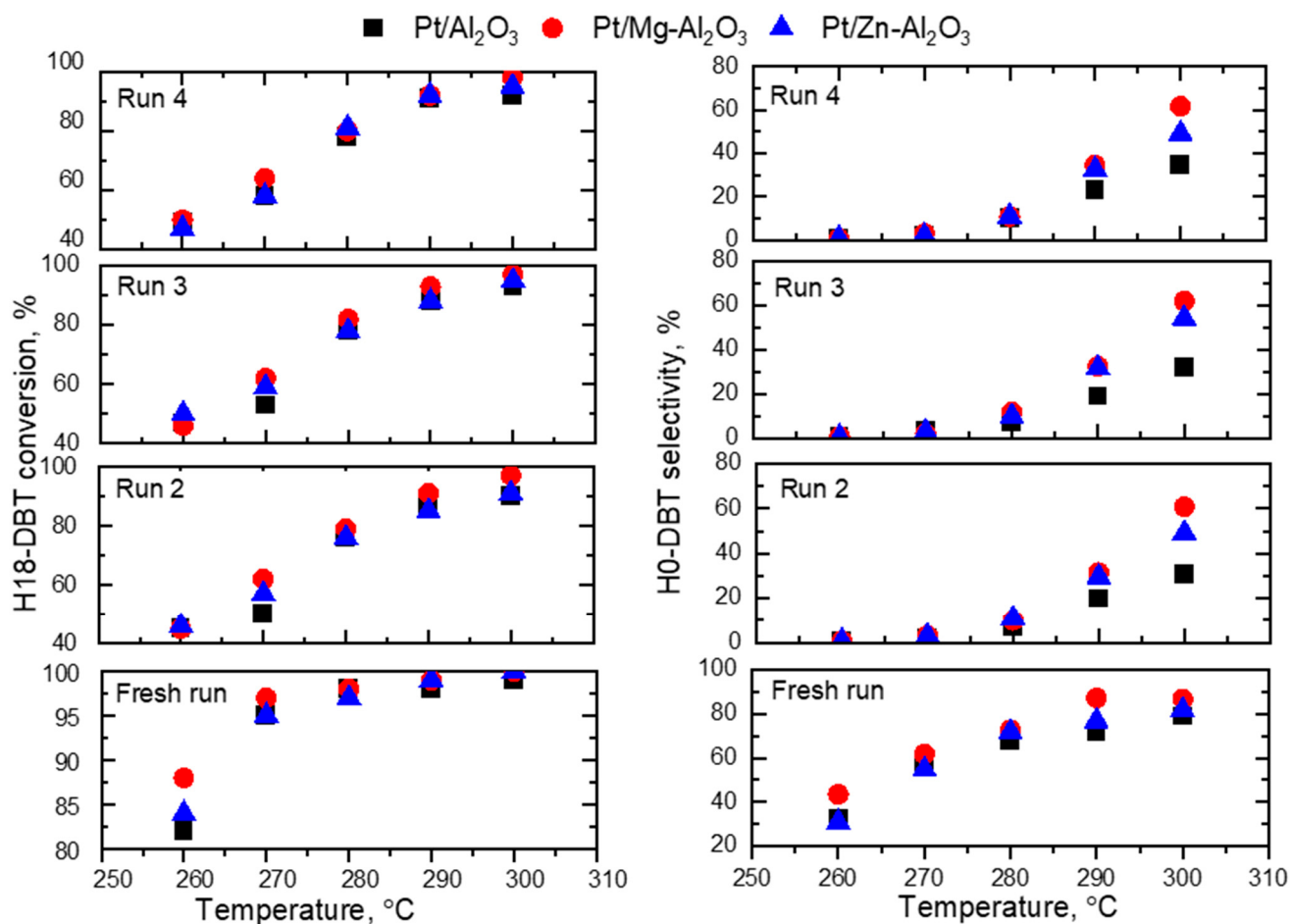


Figure 4. The H18-DBT conversion and H0-DBT selectivity vs. dehydrogenation temperature. Reaction parameters: H18-DBT, 99% doh; 0.5 wt % Pt/Al₂O₃; molar ratio of Pt to LOHC (n_{Pt}/n_{LOHC}), 0.2 mol %; temperature, 260–300 °C; reaction time, 90 min.

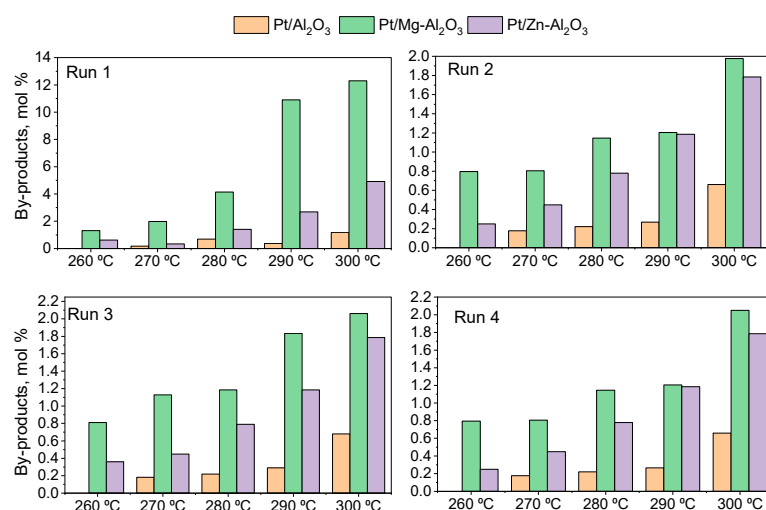


Figure 5. By-products formed during the dehydrogenation of H18-DBT in a batch reactor. Reaction parameters: H18-DBT, 99% doh; 0.5 wt % Pt/Al₂O₃; molar ratio of Pt to LOHC (n_{Pt}/n_{LOHC}), 0.2 mol %; temperature, 260–300 °C; reaction time, 6 h.

The amount of by-products increased with an increase in both the dehydrogenation temperature and the catalyst activity. By-products, in this case, are a combination of high

and low boiling point compounds, as reported in our previous work [18]. Table 1 shows that the highest amount of by-products (12 mol %) was produced by the Pt/Mg-Al₂O₃ catalyst, while Pt/Zn-Al₂O₃ and Pt/Al₂O₃ produced only 5 and 1.2 mol %, respectively, at 300 °C. In run 4, the amounts decreased to 0.68%, 2.1% and 1.9 mol % for Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃, respectively. Therefore, a decrease in the amount of by-products can be correlated with low catalytic activity observed in run 4. These by-products are due to the cracking and cyclization of dibenzyltoluene molecules and it was found that the by-products are chemically similar throughout the runs (with the only difference being the quantity). The higher the catalytic reaction, the higher the doh and the formation of aromatic molecules. These aromatic molecules are susceptible to the acidic sites of the catalyst, which provides the cracking function. A combination of side reactions leading to the formation of by-products as well as the intermediates certainly affect the selectivity to H0-DBT.

Table 1. Quantities of by-products obtained for dehydrogenation of H18-DBT using different catalysts at 300 °C.

By-Product Compounds	Category	By-Product Quantities in Mol. % per Catalyst Used		
		Pt/Al ₂ O ₃	Pt/Mg-Al ₂ O ₃	Pt/Zn-Al ₂ O ₃
Benzyltoluene (<i>m/z</i> = 182)	Low boilers	0.2	2.5	1.3
Toluene (<i>m/z</i> = 92)	Low boilers	0.01	0.3	0.2
H6-BT (<i>m/z</i> = 188)	Low boilers	0.2	1.2	0.6
Benzylmethylfluorene (<i>m/z</i> = 270)	High boilers	0.8	8.0	2.7
Total quantity (mol. %)		1.2	12	5

The formation of by-products increases with an increase in the degree of dehydrogenation over time, as shown in Figure 6. This indicates that as the dehydrogenation reaction takes place, the amount of partially and fully dehydrogenated compounds are prone to side reactions; hence, by-products are formed. In this study, the aliphatic by-products have not been obtained. Figure 7 shows possible reaction mechanisms for H0-DBT C–C bond breaking, which forms low boiling point by-products, and dehydrocyclization of H0-DBT, which forms high boiling point by-products.

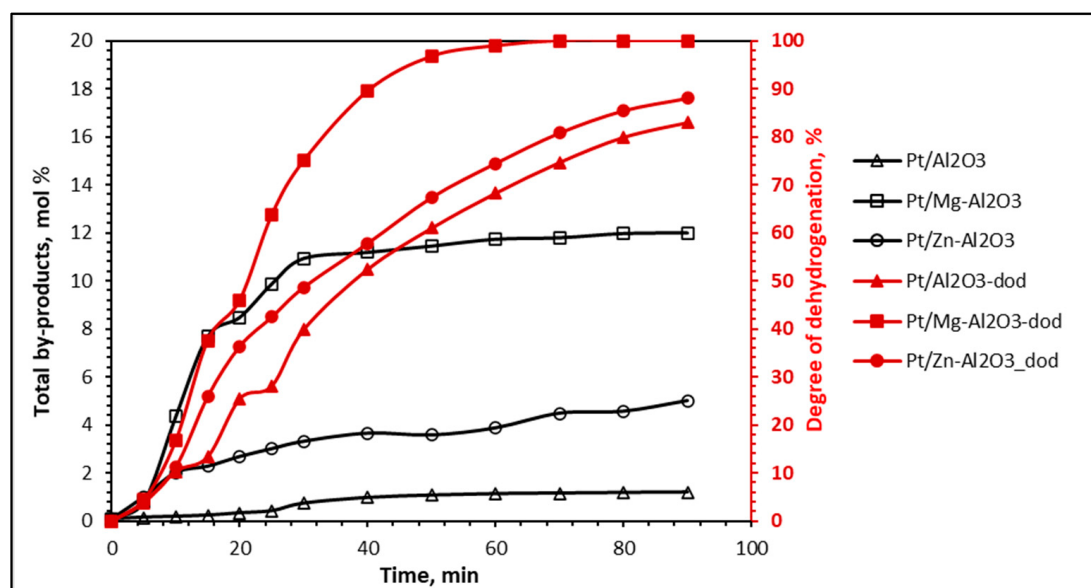


Figure 6. The evolution of by-products and the degree of dehydrogenation as a function of time using Pt/Al₂O₃, Pt/Zn-Al₂O₃ and Pt/Mg-Al₂O₃. Reaction parameters: H18-DBT, 99% doh; 0.5 wt % Pt loading; molar ratio of Pt to LOHC (nPt/nLOHC), 0.2 mol %; temperature, 300 °C.

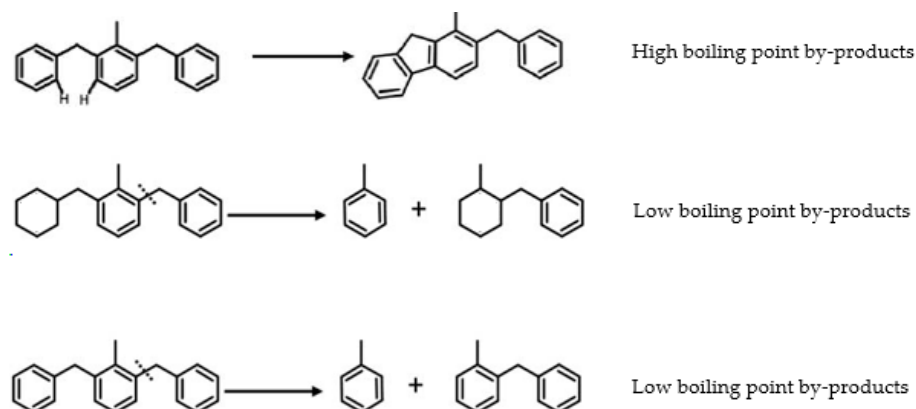


Figure 7. Possible side reaction pathways for the formation of by-products.

The deactivation parameter, $X = (X_i - X_f)/X_i \times 100$, was calculated based on the H18-DBT conversion to determine the percentage deactivation based on the reaction time of 6 h (four runs of 90 min per run). Figure 8 shows the percentage deactivation of the catalysts at 300 °C. The undoped Pt/Al₂O₃ had the highest deactivation of 7.4%, while Zn-doped and Mg-doped catalysts had deactivations of 4.9% and 1.9%, respectively. This suggests that Mg doping suppresses deactivation in a batch reactor, hence leading to an improved performance.

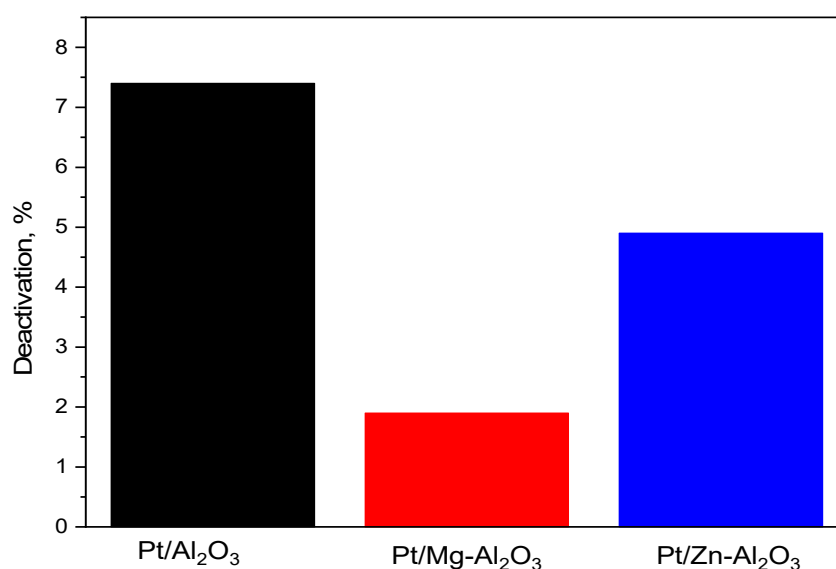


Figure 8. Catalyst deactivation in a batch reactor. Reaction parameters: H18-DBT, 99% doh; 0.5 wt % Pt/Al₂O₃; molar ration of Pt to LOHC (n_{Pt}/n_{LOHC}), 0.2 mol %; temperature, 300 °C; time, 6 h.

A summary of the performance of catalysts in a batch reactor is presented in Table 2. The highest activity for all catalysts was observed at 300 °C. At this temperature, the addition of Mg and Zn dopants significantly increased activity, conversion, selectivity and by-products. For example, the doh improved from 82 to 88% for Zn-doped Pt/Al₂O₃ and from 82 to 100% for Mg-doped Pt/Al₂O₃. Moreover, full dehydrogenation was achieved within 75 min when using the Mg-doped catalysts, whereas undoped and Zn-doped catalysts did not result in full dehydrogenation within 90 min. For all catalysts, a decrease in activity was observed after the first run. The loss of activity can be attributed to catalyst deactivation. The better performance of the Pt/Mg-Al₂O₃ catalysts can be explained by the low deactivation parameter of 1.9%, which suggests that Mg reduced deactivation. Characterization results obtained from our previous work [13] indicate that Mg reduced the acidity of alumina by 37% and this could have led to better performance than in the cases

of Zn-doped and undoped catalysts with similar acidity values (see Table 2). The strong acidic sites inhibit the desorption of products; hence, the ability of Mg to decrease these sites led to improved selectivity to H0-DBT and the ultimate enhancement of performance. Due to the high catalytic activity of Pt/Mg-Al₂O₃, a high amount of by-products were observed. Therefore, in this study, Pt/Mg-Al₂O₃ showed improved catalytic performance for the dehydrogenation of H18-DBT compared to Pt/Al₂O₃ and Pt/Zn-Al₂O₃. This study is an extension of our previously published work and the physicochemical properties of the catalysts studied in this work can be obtained from our previous work [13].

Table 2. Summary of the effects of Mg and Zn dopants on Pt/Al₂O₃ for the H18-DBT dehydrogenation performance at 300 °C in a batch reactor.

Catalyst	Dod _i	Dod _{run 4}	P _i P _{run 4} (gH ₂ /g _{Pt} /min)		S _i	S _{run 4}	X _i	X _{run 4}	ΔX
Pt/Al ₂ O ₃	82	50	1.62	0.53	79	35	99.3	92	7.4
Pt/Mg-Al ₂ O ₃	100	73	1.84	0.58	87	62	99.9	98	1.9
Pt/Zn-Al ₂ O ₃	88	60	1.68	0.55	82	49	99.9	95	4.9

X_i and X_{run 4} are the initial and final H18-DBT conversions (%), S_i and S_{run 4} are the initial and final H0-DBT selectivities (%), P_i and P_{run 4} are initial and final productivities, Y_i and Y are the initial and final dod (%), X is the deactivation parameter (%), acidity is in mmol NH₃/g_{cat}.

2.2. Reaction Kinetics for Dehydrogenation of H18-DBT

The effects of temperature on the kinetic parameters (e.g., reaction rate, rate constant, TOF) were then investigated. Experiments were conducted at dehydrogenation temperatures in the range of 260–290 °C and the dod was <70%. This was to avoid back-reactions that occur at high conversions [20].

As depicted in Figure 9, the concentration of H18-DBT decreased with time for all catalysts and the decrease in H18-DBT concentration is a function of temperature. Hence, the concentration gradient becomes steeper with an increase in temperature. At 300 °C, a H18-DBT concentration of 0.84 M was observed for Pt/Mg-Al₂O₃, while Pt/Zn-Al₂O₃ and Pt/Al₂O₃ generated final concentrations of 1.30 and 1.42 M, respectively.

From Equation (5), the rate constants (*k*), initial rate of reactions (*r*) and turnover frequencies (TOF) can be calculated using the Equations (1) and (2), as reported by Sotoodeh [28].

TOF is defined as the number of reactant molecules converted by each Pt molecule per unit time.

$$r = k \times C_0 \quad (1)$$

$$TOF = \frac{k \times Mwt_{Pt} \times C_0}{M_{Pt} \times D} \quad (2)$$

Here, *r* is the initial rate of reaction (M min^{−1} g_{cat}^{−1}), *k* is the rate constant (min^{−1}), *C*₀ is the initial concentration of H18-DBT (M), *Mwt_{Pt}* is the molecular mass of Pt (g/mol), *M_{Pt}* is the Pt loading (wt %) and *D* is the Pt dispersion (%).

The dehydrogenation kinetics of H18-DBT followed first-order reaction kinetics, as seen by the linear fit of ln (*C/C*₀) vs. time in Figure 10. This is in accordance with the literature [12,18]. Rate constants were obtained from the slopes of the respective curves and then used to calculate the rates of reaction and TOFs, as shown in Table 3. The activity increases with an increase in temperature. This is due to the collision of molecules induced by high temperatures, which then increases the reaction rate. Undoped Pt/Al₂O₃ produced higher rate constants at low temperatures (260 and 270 °C) than Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃. In specific, at 260 °C, Pt/Al₂O₃ generated a rate constant of 0.00180 min^{−1}, while Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ generated rate constants of 0.00140 and 0.00170 min^{−1}, respectively. However, at temperatures > 280 °C, this changed drastically; the activity of the doped catalysts, particularly with Mg, increased from 0.0049 to 0.0137 min^{−1}. The TOF

followed a similar trend. A high TOF value indicates a high activity due to an increase in the number of available active sites for the reaction. A Mg-doped catalyst exhibited the highest activity, i.e., a TOF of 586 min^{-1} , which is more than double compared to the Zn-doped catalyst (269 min^{-1}) and almost three times than that obtained with an undoped catalyst (202 min^{-1}) (calculated for dehydrogenation reactions at 300°C).

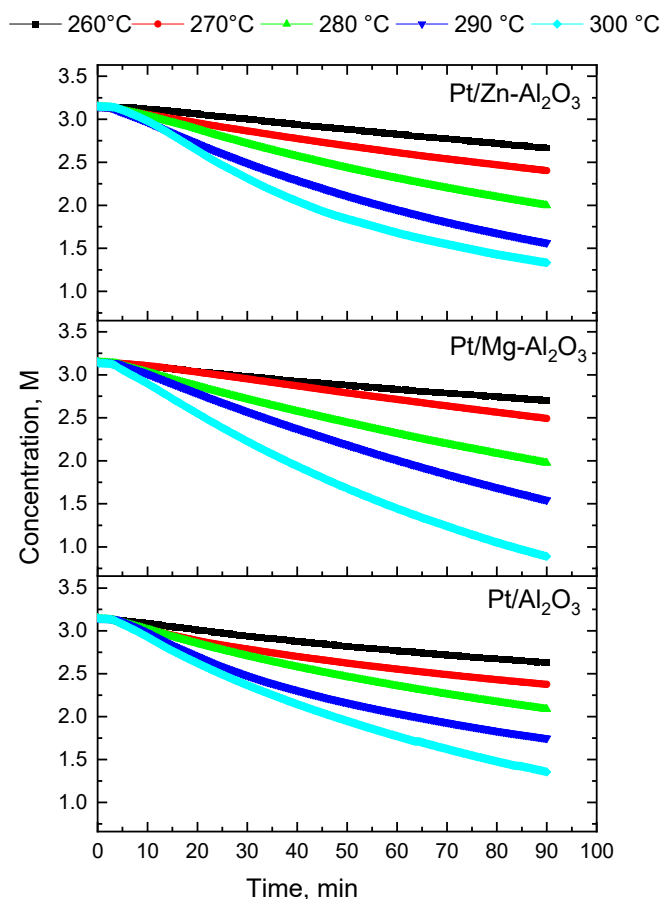


Figure 9. The change in concentration of H18-DBT versus time for Pt/Al₂O₃ catalysts in a batch reactor. Reaction parameters: H18-DBT, 99% doh; 0.5 wt % Pt; $n_{\text{Pt}}/n_{\text{LOHC}}$ (molar ratio of Pt to H18-DBT), 0.2 mol %; temperature, 260–300 °C; reaction time, 90 min.

The activation energy of the catalysts was calculated using the Arrhenius model, where the graph of $\ln k$ vs. $1/T$ is plotted (see Figure 11). The slope of the graph provided activation energies of 102, 130 and 151 kJ/mol for Pt/Al₂O₃, Pt/Zn-Al₂O₃ and Pt/Mg-Al₂O₃, respectively (see Table 4). A comparison indicates that our results are within the range reported in the literature. The regression was found to be >0.99 for all catalysts. Pt/Al₂O₃ had the lowest activation energy but low catalytic performance when compared to its counterparts (Pt/Zn-Al₂O₃ and Pt/Mg-Al₂O₃). This suggests that factors such as mass transfer limitations could have had an impact because a lower activation energy indicates that a reaction barrier is reduced and the reaction can proceed more rapidly. Interestingly, the pre-exponential factor, which indicates the frequency of the H18-DBT molecule encountered on the active sites, is directly proportional to the activation energy. The high pre-exponential factor associated with Pt/Mg-Al₂O₃ suggests an increase in the number of active sites. If the active sites are less effective (lower energy), then this decrease in energy of the active sites would lead to a growth in the activation energy [29]. The high activation energy observed for Pt/Mg-Al₂O₃ means more energy was used to overcome the reaction barrier when using this catalyst. Jorschick et al. argue that this high activation energy indicates that mass transfer effects have no dominant effect in the dehydrogenation reaction under the used conditions [30].

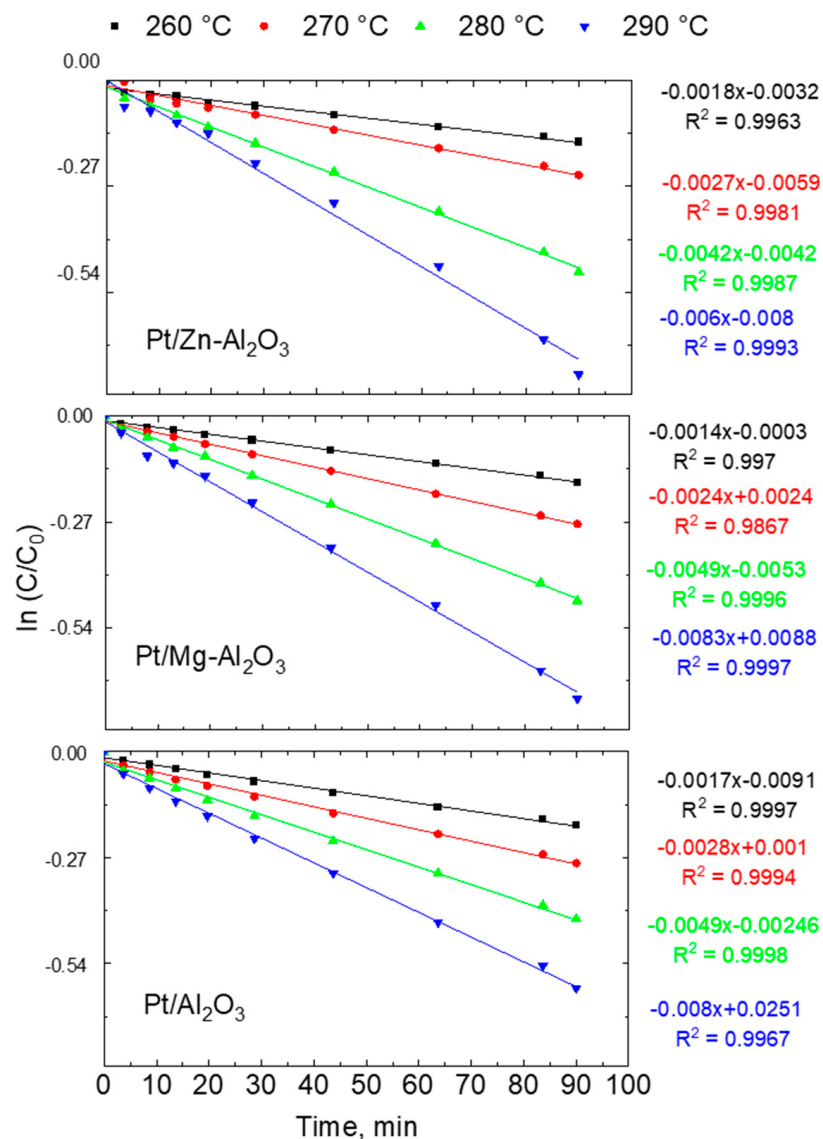


Figure 10. First-order reaction kinetics of Pt/Al₂O₃ catalysts during H18-DBT dehydrogenation between 260 and 290 °C.

Table 3. Rate constants, initial rates of reaction and TOF of H18-DBT dehydrogenation using Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ catalysts between 260 and 300 °C.

Catalyst	Temp, °C	k, (min ⁻¹)	Initial Rate of Reaction (M min ⁻¹ g _{cat} ⁻¹)	TOF (min ⁻¹)
Pt/Al ₂ O ₃	260	0.00180	0.02352	47
	270	0.00270	0.03696	70
	280	0.00420	0.05376	109
	290	0.00600	0.08064	155
	300	0.00780	0.09702	202
Pt/Mg-Al ₂ O ₃	260	0.00140	0.01806	61
	270	0.00240	0.03150	103
	280	0.00490	0.06258	209
	290	0.00830	0.09996	355
	300	0.01370	0.17640	586
Pt/Zn-Al ₂ O ₃	260	0.00170	0.02016	49
	270	0.00280	0.03318	81
	280	0.00490	0.05999	142
	290	0.00800	0.09576	231
	300	0.00930	0.10836	269

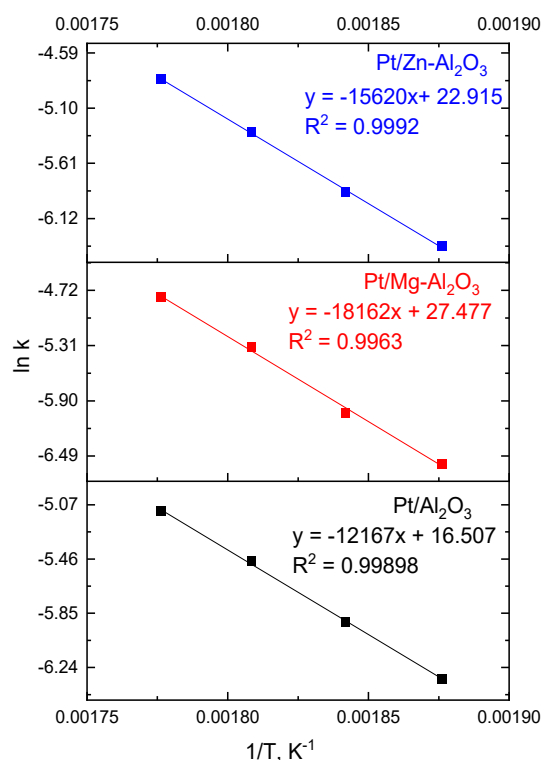


Figure 11. Arrhenius plot for the dehydrogenation of H18-DBT between 260 and 290 °C.

A similar trend was observed by Seidel [16]: the dehydrogenation of H18-DBT at 270–320 °C with 0.5 wt % Pt/Al₂O₃, 0.3 wt % Pt/Al₂O₃ and 0.3 wt % Pt/Al₂O₃ (0.14 wt % S) generated activation energies of 97, 131 and 143 kJ/mol, respectively. High activation energies (131 and 143 kJ/mol) for catalysts with large pore diameter (24.6 nm) were obtained (compared with 97 kJ/mol for a pore diameter 3.2 nm). Therefore, the addition of Mg and Zn dopants reduced the diffusion barrier, as evidenced by the low activation energy (102 kJ/mol) of the undoped catalyst. Mg also increases basic surface OH groups on catalysts, which enhances fast kinetics, as evidenced by the work of Kim et al. [31]. The Ru/MgO catalysts had better activity and kinetics compared with Ru/Al₂O₃ during the hydrogenation of benzyltoluene because of the low surface acidity of the MgO support. We are thus able to confirm the higher catalytic activity of the Mg-doped catalyst compared with the other catalysts considered here. Since the catalysts studied here had the same textural properties (see Table 2), the ability of the Mg catalyst to slightly suppress pore size reduction may have contributed to improved performance. Optimal Mg loading could further contribute to the retention of the pore size and subsequently result in better performance.

Table 4. Comparison of kinetic parameters of Pt/Al₂O₃ catalysts between this study and the literature.

Reference	Reactor Type	Catalyst	Conditions	Kinetic Values		
				n	k ₀	E _a
This study	Batch	0.5 wt % Pt/Al ₂ O ₃	260–290 °C; 0.2 mol %	1	1.77×10^7	102
		0.5 wt % Pt/Mg-Al ₂ O ₃		1	2.30×10^{11}	151
		0.5 wt % Pt/Zn-Al ₂ O ₃		1	1.15×10^{10}	131
[12]	Batch	1 wt % Pt/Al ₂ O ₃	260–290 °C; 0.4 mol %	1	2.21×10^{16}	205
		1 wt % Pd/Al ₂ O ₃		1	2.26×10^4	84
		1 wt % Pt-Pd/Al ₂ O ₃		1	2.35×10^2	66
[18]	Batch	1 wt % Pt/Al ₂ O ₃	300–355 °C; 0.2 mol %	1	1.76×10^{16}	201
[19]	Fixed bed	0.3 wt % Pt/Al ₂ O ₃	280–300 °C, 1 bar (2.5 bar)	2	6.49×10^5 (2.66×10^8)	117 (149)

Table 4. Cont.

Reference	Reactor Type	Catalyst	Conditions	Kinetic Values		
				n	k ₀	E _a
[15]	Batch	0.3 wt % Pt/TiO ₂	270–310 °C; 0.1 mol %	1.66	6.16 × 10 ⁹	145
		0.3 wt % Pt (0.1 wt % S)/TiO ₂	270–310 °C; 0.1 mol %	1.51	3.23 × 10 ¹²	174
[22]	Fixed bed	Pt/Al ₂ O ₃	260–310 °C	1	125 s ^{−1}	120
[20]	Pd/Ag membrane	Pt/Al ₂ O ₃	300–350 °C	1	2.637 × 10 ^{−6} m ³ /kg _{cat} ·s	156 ± 28.5
[32]	Batch	0.3 wt % Pt/Al ₂ O ₃	280–310 °C; 0.05 mol %; di 11 nm	-	1.60 × 10 ¹⁰	151
		0.3 wt % Pt/Al ₂ O ₃	280–310 °C; 0.05 mol %; di 14 nm	-	1.50 × 10 ¹¹	161
		0.3 wt % Pt/Al ₂ O ₃	280–310 °C; 0.05 mol %; di 18 nm	-	1.30 × 10 ¹²	169
[21]	Batch	0.5 wt % Pt/Al ₂ O ₃	270–320 °C; 0.05 mol %	1.84	8.30 × 10	97
		0.3 wt % Pt/Al ₂ O ₃	270–320 °C; 0.05 mol %	2.21	2.27 × 10 ⁴	131
		0.3 wt % Pt (0.14 wt % S)/Al ₂ O ₃	270–320 °C; 0.05 mol %	1.62	6.76 × 10 ⁶	143
[23]	Fixed bed	5 wt % Pt/Al ₂ O ₃	250–320 °C; WHSV > 2 h ^{−1}	2.35–2.44	5.40 × 10 ¹¹	171
[8]	Microchannel reactor	2 wt % Pt/Al ₂ O ₃	260–320 °C; 0.01 mL/min	1	3.2725 s ^{−1}	13.79

n is the order of reaction, k₀ is the frequency or pre-exponential factor in min^{−1} and E_a is the activation energy in kJ/mol.

3. Characterization

This study is a continuation of the previous work already published, where methods and detailed characterization of the catalysts used in this study can be found in the reported literature [13]. Characterization techniques, such as CO pulse chemisorption, Hydrogen temperature programmed reduction (H₂-TPR), Ammonia temperature programmed desorption (NH₃-TPD), transmission electron microscopy (TEM) and inductively coupled plasma-optical emission spectrometry (ICP-OES) are described in our previous study. The Pt dispersion percentage, a critical factor for catalytic efficiency, is highest in Pt/Al₂O₃ (38%), indicating a better spread of platinum particles across the support. However, the Mg-doped catalyst (34% dispersion) outperformed a highly dispersed Pt/Al₂O₃. Therefore, a 4% difference in dispersion has not led to a significant change in catalyst performance. Despite differences in dispersion, both Pt/Al₂O₃ and Pt/Mg-Al₂O₃ show identical metallic surface areas (0.42 m²/g), suggesting that the metallic surface area is not a determining factor for the improved performance shown by Pt/Mg-Al₂O₃. The hydrogen consumption values could also reflect the catalytic activity, which is notably higher for Pt/Mg-Al₂O₃ (64 μmol/g) and Pt/Zn-Al₂O₃ (55 μmol/g). High hydrogen consumption in TPR indicates the presence of a significant amount of reducible metal oxides, which in a metallic state are responsible for the catalytic activity. There is a slight variation in total acidity observed among the three catalysts, with marginally higher acidity in Pt/Zn-Al₂O₃. Particle size has an impact on the surface area and reaction kinetics, and Pt/Zn-Al₂O₃ exhibits slightly smaller particles with a 0.06–0.08 nm difference. The consistency in Pt loading across the catalysts is notable, but Mg and Zn dopants present in the latter two suggest a modification in electronic or structural properties, which can considerably affect catalytic performance already discussed. Thus, a comparison depicted in Table 5 emphasizes the importance of choosing a catalyst based on the specific requirements of the H18-DBT dehydrogenation process.

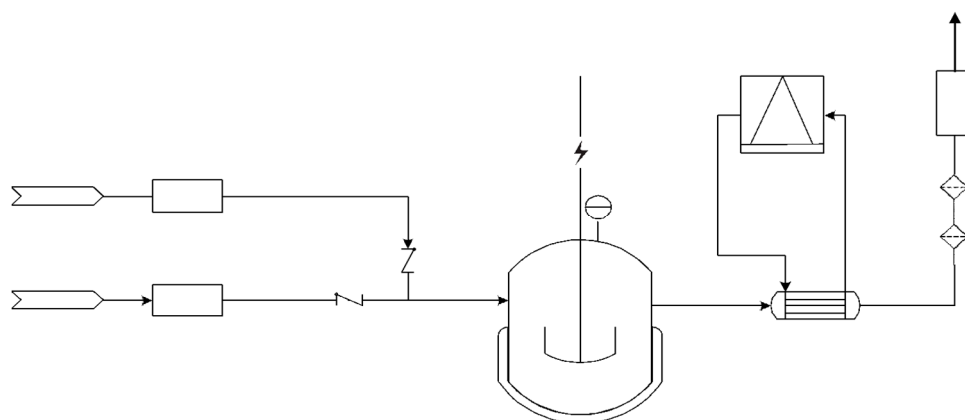
Table 5. Catalyst properties determined by various characterization techniques.

Catalyst Properties	Pt/Al ₂ O ₃	Pt/Mg-Al ₂ O ₃	Pt/Zn-Al ₂ O ₃
^a Pt dispersion, %	38	34	23
^a Metallic surface area, m ² /g _{sample}	0.42	0.42	0.28
^b H ₂ consumption, μmol/g	34	64	55
^c Total Acidity, NH ₃ /g _{cat}	0.48	0.41	0.49
^d Particle size, nm	1.72	1.70	1.54
^e Pt loading, wt%	0.48	0.49	0.48
^e Dopant loading, wt %		3.89	3.44

^a CO pulse chemisorption. ^b H₂-TPR. ^c NH₃-TPD. ^d TEM. ^e ICP-OES.

4. Experimental

The modified Pt-based catalysts (Pt/Al₂O₃, Pt/Mg-Al₂O₃, Pt/Zn-Al₂O₃) were prepared following the wet impregnation method as described, characterized and analyzed in our previous work [8]. A batch reactor setup, as shown in Figure 12, was used to study the reaction kinetics for the dehydrogenation of H18-DBT. A more detailed description of the experimental setup was reported earlier by our research team [16].

**Figure 12.** Schematic representation of a batch reactor setup used for dehydrogenation experiments [6].

The degree of dehydrogenation (dod) obtained was calculated based on the total hydrogen produced vs. theoretical hydrogen stored in H18-DBT. This value was confirmed by determining the dod of the remaining reaction mixture using a calibrated refractometer. The dod, productivity (P) and concentration (C) were calculated using Equations (3), (4) and (5), respectively.

$$Dod (\%) = \frac{\text{Volume of H}_2 \text{ released}}{\text{Theoretical H}_2 \text{ volume}} \times 100 \quad (3)$$

$$P = \frac{m_{H_2}}{m_{Pt} \cdot t} \quad (4)$$

$$C_{H18-DBT} = \frac{n_{H18-DBT} \left(1 - \frac{\text{Yield} (\%)}{100} \right)}{V_{Total}} \quad (5)$$

where m , n and V_{Total} are the mass (g), number of moles and total volume (L) of the liquid, respectively.

5. Conclusions

The evaluation of the catalytic performance of Mg- and Zn-modified Pt/Al₂O₃ catalysts in a batch reactor indicated a strong dependence of activity and performance on temperature. The highest activities were obtained at 300 °C for all catalysts. The Pt/Mg-Al₂O₃ was the best-performing catalyst with dod, productivity, conversion and selectivity

of 100%, 1.84 gH₂/g_{Pt}/min, 99.9% and 87%, respectively. After run 4, the catalytic activity for all catalysts decreased due to catalyst deactivation. The extent of deactivation, expressed as a deactivation parameter, indicated that Mg reduced the deactivation of Pt/Al₂O₃ by a factor of three, which then led to improved stability and better performance. The presence of by-products was a function of catalyst activity. Mg-doped catalysts performed better because of their favourable acidity feature, which suppressed deactivation and facilitated easy diffusion of reactants and products (high activation term), thus resulting in better catalytic activity. The dehydrogenation activity of H18-DBT followed first-order reaction kinetics. The obtained activation energy of Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ were 101, 151 and 131 kJ/mol, respectively. In this case, a high number of active sites corresponds to a high frequency factor value, which relates to high activation energy. Therefore, a lower activation energy for the dehydrogenation of H18-DBT will not always produce a high reaction rate. The high activation energy of the doped catalysts, particularly Pt/Mg-Al₂O₃, suggests that mass transfer effects have no dominant effect in the dehydrogenation reaction under the used conditions. The catalysts in stable form meet the set criteria in terms of H18-DBT conversion (>90%). However, there is a need for further improvement since the catalyst productivity and selectivity do not meet the set criteria provided in the introduction section.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal14010032/s1>, Figure S1: The effect of Mg and Zn dopants on the hydrogen flow and yield in a batch reactor. Reaction parameters as a function of dehydrogenation temperature in a batch reactor. Reaction parameters: H18-DBT, 99% doh; 0.5 wt % Pt; nPt/nLOHC, 0.2 mol %; temperature, 300 °C; time, 90 min.

Author Contributions: Conceptualization, P.M. and D.B.; Methodology, R.G.; Formal analysis, R.G.; Data curation, R.G.; Writing—original draft, R.G. and P.M.; Supervision, P.M. and D.B.; Project administration, D.B.; Funding acquisition, D.B. All authors have read and agreed to the published version of the manuscript.

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