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Moving from Batch to Continuous Operation for the Liquid Phase Dehydrogenation of Tetrahydrocarbazole

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S Supporting Information

ABSTRACT: Despite the numerous advantages of continuous processing, high-value chemical production is still dominated by batch techniques. In this paper, we investigate options for the continuous dehydrogenation of 1,2,3,4-tetrahydrocarbazole using a trickle bed reactor operating under realistic liquid velocities with and without the addition of a hydrogen acceptor. Here, a commercial 5 wt % Pd/Al_2O_3 catalyst was observed to slowly deactivate, hence proving unsuitable for continuous use. This deactivation was attributed to the strong adsorption of a byproduct on the surface of the support. Application of a base washing technique resolved this issue and a stable continuous reaction has been demonstrated. As was previously shown for the batch reaction, the addition of a hydrogen acceptor gas (propene) can increase the overall catalytic activity of the system.

1. INTRODUCTION

Motivated by a desire for flexibility, liquid phase processing of fine chemicals occurs largely under batch operation, allowing use of installed equipment for a wide variety of reactions. It is generally considered that the initial capital costs are also relatively low when compared to continuous operation and installation is relatively simple, meaning that, if necessary, additional capacity can be easily accommodated by numbering-up or scaling out. However, the time required for starting up each batch reaction and the subsequent downtime including cooling as well as post reaction cleanup can be longer than the reaction time itself, resulting in significant loss of manufacturing time and increased labour.

Conversely, continuous operation occurs under steady state for extended times, thereby requiring smaller equipment and facilities as well as less labour and downtime. With decreased manual input, there is also a reduced chance for exposure to risk, leading to improved process safety particularly in cases where toxic, flammable, or explosive materials are used. Decreasing start-up and cool-down cycles also reduces the time required to produce a given campaign, resulting in savings in both energy and materials when compared to a batch process. Furthermore, the more stable and consistent reaction conditions generally result in a higher quality product when compared to batch production.

Rode et al. demonstrated the advantages of continuous processing for the selective hydrogenolysis of glycerol to 1,2-propanediol, where the conversion and selectivity to the desired product increased from 34% to 65% and 84% to over 90%, respectively,[1] on changing from batch to continuous packed bed operation. These improvements in rate and selectivity were attributed to a number of factors including in situ catalyst activation and suppression of side reactions from a lower contact time. A factor of 3 decrease in the contact time afforded by continuous operation was also observed to improve the selectivity for the dehydration of glycerol to acetol from 55% to 70%.[2]

While not all liquid phase processes are suitable for conversion from batch to continuous operation, there are cases where a larger scale fine chemical process could benefit from being run continuously. To determine when continuous operation would be advantageous, Calabrese and Pissavini compiled a table of guidelines for initial assessment of flow reactor applicability, in which severe reaction conditions such as pressures greater than 120 bar, temperatures less than −10 °C, formation of toxic byproducts, highly exothermic reactions, and sequential reactions reducing product selectivity amongst others are given as reasons to consider use of a flow reactor.[3] Anderson discussed similar advantages amongst others for continuous operation for the production of pharmaceutical materials, citing improved control of mixing and heat transfer, more facile operation for both cryogenic and high-temperature processes, removal of reactive intermediates resulting in improved selectivity, and the removal of toxic compounds.[4] Further discussion on the topic of batch to continuous processing is given in the article by Stitt and Rooney.[5]

Herein we expand on our work on the dehydrogenation of 1,2,3,4-tetrahydrocarbazole (THCZ) by investigating the liquid phase dehydrogenation reaction under continuous operation using a trickle bed reactor (TBR).

Carbazoles can be produced from coal tar and crude oil or through synthetic routes such as the Graebe−Ullmann reaction[6] and the liquid-phase dehydrogenation of 1,2,3,4-

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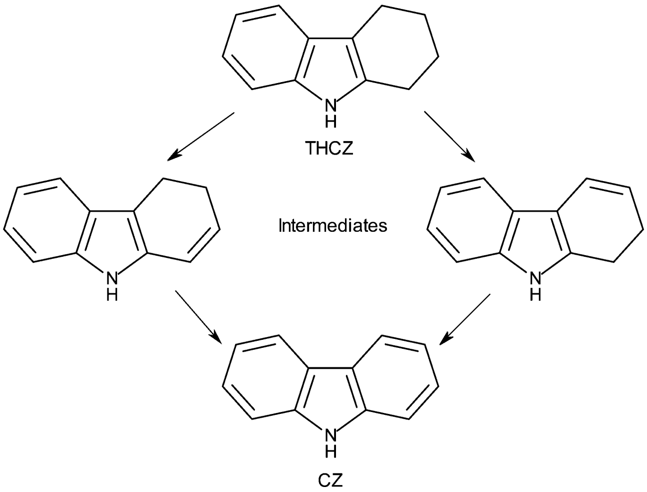
tetrahydrocarbazole obtained from the Borsche−Drechsel synthesis.[7] The dehydrogenation has been facilitated over a range of metal catalysts such as nickel, palladium, and unsupported molybdenum carbide.[8] Carbazoles are well-known chemical intermediates, used in the synthesis of pharmaceuticals, agrochemicals, dyes, pigments, and other organic compounds. Substituted carbazoles have been used for optical applications,[9] and many others are biologically active[10] with their alkaloid derivatives having antitumor, antibacterial, antimicrobial, and anti-inflammatory properties.[11] More recently hydrocarbazoles have been investigated as potential materials for on-board organic hydrogen storage.[12] Dehydrogenation of dodecahydro-*N*-carbazole to tetrahydrocarbazole and on to carbazole has been highlighted as a potential system for this application; however, low reaction rates attributed to strong adsorption of the substrate and products have been observed. In contrast, dehydrogenation of dodecahydro-*N*-ethylcarbazole is considerably faster than dodecahydro-*N*-carbazole as the ethyl group causes a steric hindrance, preventing the strong adsorption of the organic materials on the catalyst surface.[13] However, decomposition of dodecahydro-*N*-ethylcarbazole by loss of the ethyl group at temperatures greater than 350 K[14] as well as the lower hydrogen storage capacity of 5.8 wt % compared to 6.7 wt % for dodecahydro-*N*-carbazole[15] maintains interest in developing a dehydrogenation catalyst to form the unsubstituted carbazole.

Previously, we reported both increased yields and selectivities for the dehydrogenation of tetrahydrocarbazole to carbazole (CZ) using a commercial 5 wt % Pd/Al_2O_3 catalyst with the addition of propene into the stirred tank reactor (STR) (Scheme 1).

Scheme 1. Reaction Scheme for the Dehydrogenation of Tetrahydrocarbazole



It was observed that the reaction was limited by the build-up of hydrogen within the pores of the catalyst, which favored the hydrogenation of the intermediate product to form the initial starting material. By adding a gaseous phase hydrogen acceptor, such as propene, the hydrogen within the catalyst pores was rapidly reacted out of the system, allowing the reaction to proceed to completion at a significantly faster rate.[16]

DFT calculations and kinetic isotope effect experiments indicated that although the product adsorbed more strongly in the gas phase calculations, in the presence of the solvent, the reaction was controlled by the first dehydrogenation step.[17]

The above results suggest that the dehydrogenation of 1,2,3,4-tetrahydrocarbazole would be a relevant, useful, and challenging test molecule to demonstrate the potential for continuous dehydrogenation in the fine chemical industry.

2. EXPERIMENTAL SECTION

2.1. Catalysts and Materials. Tetrahydrocarbazole (TCHZ) (99%) and mesitylene (97%) were purchased from Aldrich and used as received. All gases were purchased from BOC and were of greater than 99% purity. The 5 wt % Pd/Al_2O_3 catalysts used throughout this work were commercially available catalysts obtained from Johnson Matthey as either a powder (Al_2O_3 type 324, particle size 20 μm) or eggshell cylindrical pellets of nominal 3 mm size (Al_2O_3 type 49). Prior to use in a batch reactor, the pellets were crushed and sieved to particles of less than 75 μm. Base-washed catalysts were prepared from the pellets or crushed pellets by placing the 5 wt % Pd/Al_2O_3 (5 g) into a round-bottomed flask with a 0.1 M aqueous solution of lithium hydroxide, sodium hydroxide, or potassium hydroxide (25 mL) and stirring for 1 to 2 h before leaving overnight. The catalysts were removed by filtration and washed with water until a neutral pH was obtained before drying in an oven at 110 °C overnight. These treated catalysts were labelled 5 wt % Pd/Al_2O_3 (Li, Na, or K), indicating the base which was used to treat the 5 wt % Pd/Al_2O_3.

The 5 wt % Pd/C catalyst was also a commercial catalyst obtained from Johnson Matthey. The 5 wt % Pd/α-Al_2O_3 catalyst was prepared on an alpha alumina support, purchased from Alfa Aesar, by wet impregnation using an aqueous solution of palladium nitrate containing nitric acid. After drying overnight at 120 °C, the catalyst was calcined at 500 °C under a flow of air for 3 h and reduced in a H_2 flow at 400 °C for 5 h[18] with argon used to purge the catalyst before and after reduction for 15 min.

2.2. Catalyst Characterisation. The catalysts were characterised by a range of techniques and the characterisation data is summarised in Table 1. BET N_2 isotherms (Micromeritics ASAP 2010) were used to determine the surface area and pore volumes whilst the metal loading was measured by ICP-OES (Perkin-Elmer Optima 4300). The metal dispersion of each catalyst was determined by CO chemisorption, which required the catalysts to be reduced at 150 °C in 5% H_2/Ar and cooled to room temperature in He before pulses of CO (2.38 × 10^{-6} mol) were passed over the catalyst until saturated. The metal dispersion was calculated, assuming a Pd:CO ratio of 1:1.

Table 1. Characterisation of the Catalysts Used for the Dehydrogenation of Tetrahydrocarbazole

catalyst	form	support particle size	BET surface area (m^2 g^{-1})	pore volume (cm^3 g^{-1})	Pd dispersion[a]
5 wt % Pd/Al_2O_3	powder	20 μm	143	0.53	22.4
5 wt % Pd/Al_2O_3	crushed 3 mm pellets	<75 μm	82	0.19	6.4
5 wt % Pd/Al_2O_3(Na)	crushed 3 mm pellets	<75 μm	103	0.24	–

[a] Pd dispersion taken from reference 16.

The total number of acidic sites (sites m^{-2}) over each catalyst was measured using the temperature-programmed desorption of pyridine.[19] This was performed by pretreating a sample of catalyst (50 mg) at 250 °C for 2 h in air before exposure to pyridine. The catalyst samples adsorbed with pyridine (15−20 mg) were heated to 600 °C, at a rate of 20 °C min^{-1} in dry N_2 at a flow rate of 40 mL min^{-1}. The mass loss due to desorption of pyridine from the acidic sites was determined as a function of the mass of the catalyst and then normalised to the surface area of the catalyst.

X-ray diffraction patterns of the powdered catalysts were obtained using Cu Kα radiation (PANalytical X'PERT PRO MPD X-ray diffractometer).

2.3. Adsorption Isotherms. Adsorption of THCZ onto untreated and sodium-hydroxide-washed 5 wt % Pd/Al_2O_3 was measured by contacting samples of 5 wt % Pd/Al_2O_3 and 5 wt % Pd/Al_2O_3(Na) (0.1 g) with solutions of THCZ in mesitylene up to a concentration of 0.03 mol m^{-3}. The mixtures were stirred at room temperature overnight before filtration to remove the catalyst with analysis of the final concentration of THCZ by GC analysis.

2.4. Catalyst Reuse. To study the deactivation of the catalyst in the STR batch system, a single batch of catalyst was reused a number of times. In this case, the catalyst was removed from the postreaction mixture by filtration and subjected to one of the following regeneration procedures. The catalyst was washed with acetone (30 mL, which was sufficient to keep all the catalyst immersed), washed in acetone overnight, washed in acetone for 10 days with the acetone removed and changed daily, and washed using a soxhlet extraction procedure again with acetone or recalcined at 500 °C for 2 h.

2.4.1. Typical STR Batch Reaction Procedure. Batch reactions were carried out in a stainless steel Parr Autoclave reactor (300 mL capacity) containing a gasifying stirrer, removable baffles, and a temperature-controlled heating jacket. The gas was sparged into the vessel, and the pressure monitored using a pressure gauge on the reactor. For a typical reaction, THCZ (2 g), mesitylene (200 mL), and 5 wt % Pd/Al_2O_3 (1 g) were placed in the reactor and a sample (1 mL) was taken for analysis by GC. The reactor was sealed and purged with 2 bar of nitrogen gas 5 times, before the reactor was heated to the reaction temperature, typically 135 °C, with moderate stirring. When at reaction temperature, the system was pressurised with propene, typically to 4 bar, at which point another sample was taken for analysis which corresponded to time zero. The reaction was started immediately by starting the impellor at typically 1200 r.p.m. Samples were taken every half hour over the first three hours followed by every hour up to a 6 h reaction time.

2.4.2. Typical TBR Batch and Continuous Reaction Procedure. The TBR was operated as a cocurrent down flow trickle bed reactor with a liquid recirculation and continuous gas feed, shown in Figure 1.

The system was designed to operate at a maximum temperature of 450 °C and a maximum pressure of 40 bar. The liquid reaction mixture was placed into a receiver vessel of a 500 mL capacity and pumped around a closed loop using a Bran + Luebe H2−31 Metering Pump (0−80 L h^{1-}, discharge pressure 40 bar). In the case of continuous operation, fresh feed was pumped into the receiver tank while an equal volume was extracted from the system. The liquid was introduced to the fixed bed using a spray nozzle, while the gas was introduced using a Brooks 5850 TR mass flow controller (0−2 L min^{-1}).

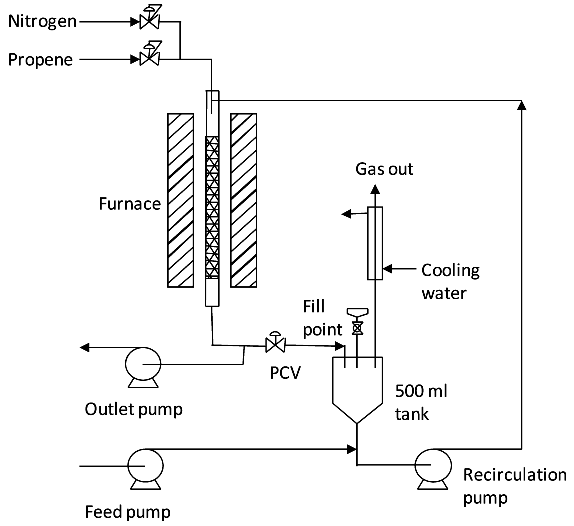


Figure 1. Schematic of the Trickle Bed Reactor.

The lines delivering liquid and gas reactants as well as the exit line and receiver vessel were heated to reaction temperature during the reaction. A pressure control valve (PCV in Figure 1) facilitated the depressurization of the reactor exit flow, allowing the liquid to be recycled to the receiver vessel and the gas vented. The temperature, gas and liquid mass flow rates and pressure were monitored on a control system.

Before reaction, the 5 wt % Pd/Al_2O_3, pellets were packed into the fixed bed of 25.4 mm internal diameter with a 3 mm diameter inert, spherical silica support, as shown in Figure S1 of the Supporting Information, after which the reactor was reconnected to the TBR system. The system was pressurised to 1 bar gauge with nitrogen to ensure no leaks were present in the system, and the catalyst bed was wetted for 1 h with the liquid reaction mixture (300 mL) consisting of THCZ (3 g) dissolved in mesitylene (300 mL) at a liquid flow rate of 196 mL min^{-1} and a gas flow rate of 100 mL min^{-1} at ambient temperature and pressure. After wetting, the liquid was discharged before the fresh reaction feed, consisting of THCZ (4 g) dissolved in mesitylene (400 mL), was added. The system was heated to the reaction temperature, typically 150 °C and pressurised with propene or nitrogen, typically to 1 bar, after the reaction temperature had been attained. Once the reaction conditions were reached, the reaction was initiated by starting the liquid flow at 167 mL min^{-1} (equivalent to a superficial velocity of 5.5 mm s^{-1}) and gas flow at 200 mL min^{-1} (equivalent to a superficial velocity of 6.6 mm s^{-1}). Samples were taken over time for analysis by GC.

The TBR was operated either under semibatch mode where all the liquid flow was circulated back into the reactor by the metering pump while the gas was vented or in continuous mode, where a portion of the liquid feed was removed from the reactor while 99.75% of the liquid was recycled. This protocol has been described by the groups of Hickman[20] and Pollington[21] to ensure complete wetting of the catalyst bed and minimisation of external mass transfer, thereby allowing reliable measurement of a rate of reaction. The inlet and outlet flow of the liquid feed were both set to 1 mL min^{-1}.

2.5. Analysis of Reaction Mixture. Analysis of the reaction mixture was carried out using a GC system equipped with an Agilent 19091J-433 HP-5 5% phenylmethylsiloxane capillary column and FID detector. The concentration of

THCZ and CZ were obtained by comparison with calibration curves prepared using pure samples. The conversion to carbazole in the reactions carried out in the batch STR and semibatch TBR was calculated according to eq 1, where C_{cz} is the concentration at any time after time zero and C_{THCZ0} is the concentration of THCZ at time zero.

$$\text{conversion of THCZ (\%)} = \frac{C_{CZ}}{C_{THCZ0}} \times 100\% \qquad (1)$$

3. RESULTS AND DISCUSSION

3.1. Kinetic Reactions Carried out in the Batch STR.

3.1.1. General Kinetic Data. The conversion of THCZ and the corresponding formation of CZ during a typical reaction are shown in Figure 2, with complete conversion of THCZ occurring after about 90 min with a selectivity to CZ of greater than 99%. Although the mass balance was low at the start of the reaction, this was recovered as the reaction proceeded with a mass balance of 97% at 98% conversion. The loss of THCZ concentration at time zero is therefore due to a combination of its adsorption onto the catalyst surface and some reaction occurring as the temperature was increased from room temperature to the reaction temperature of 135 °C.

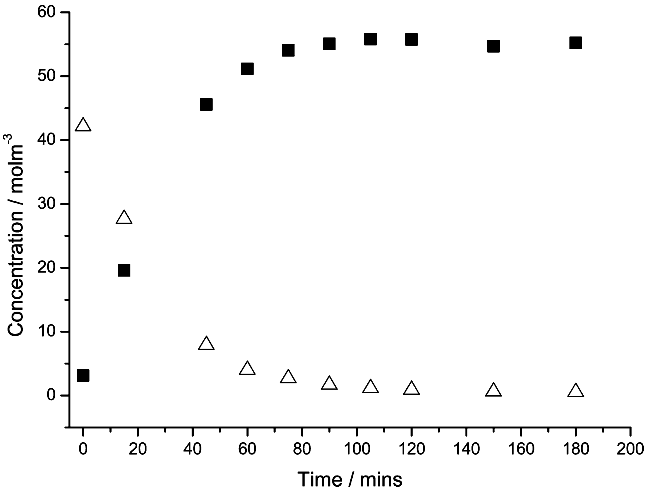


Figure 2. Typical reaction profile showing the dehydrogenation of THCZ (△) to CZ (■). Reaction conditions: the reaction was carried out over 5 wt % Pd/Al_2O_3 powder (1 g) with THCZ (2 g) in mesitylene (200 mL) at 135 °C and 4 bar propene.

Fitting of reaction equations to the data showed the reaction to be initially close to zero order with respect to THCZ and then positive order as the conversion is increased (Figure S2 of the Supporting Information). This was supported by just over a 2-fold increase in initial rate from 1.79×10^{-4} mol min^{-1} g_{cat}^{-1} to 4.78×10^{-4} mol min^{-1}g_{cat}^{-1} when the THCZ concentration was increased by 5-fold from 0.058 to 0.29 M. This is in agreement with kinetic data reported previously,[16] which also describes the optimisation of this system in terms of the solvent and hydrogen acceptor. To gain a better understanding of the system before moving from batch to continuous operation, the effects of the catalyst form and potential deactivation was studied using the batch STR.

3.1.2. Catalyst Form. Comparison of the reaction profile over the 5 wt % Pd/Al_2O_3 powdered catalyst of particle size 20 μm with a 5 wt % Pd/Al_2O_3 pellet catalyst crushed to less than 75 μm shows that the lower surface area of the crushed pellets, 82 m^2 g^{-1} compared to 143 m^2 g^{-1} of the powder, as well as the larger particle size of the pelletized catalyst results in a decreased initial rate of reaction from 1.79×10^{-4} mol min^{-1} g_{cat}^{-1} to 6.94×10^{-5} mol min^{-1} g_{cat}^{-1} (Figure 3). Previous studies on this system showed the rate of reaction to depend strongly on the catalyst particle size. As was reported previously when the catalyst was crushed and sieved to give three different particle size ranges, the resulting reaction rates decreased with increasing particle size and followed a linear relationship with the ln (average particle diameter),[16] indicating that the reaction was under an internal (pore) diffusion limitation. The decrease in reaction rate using the crushed pellets shown here is attributed to a combination of increased internal diffusion and the decreased dispersion of the palladium 6.4% on the eggshell pellets compared to 22.4% on the powder. Given this result, internal mass transfer limitation is expected to be present in the 3 mm pellets used within the TBR.

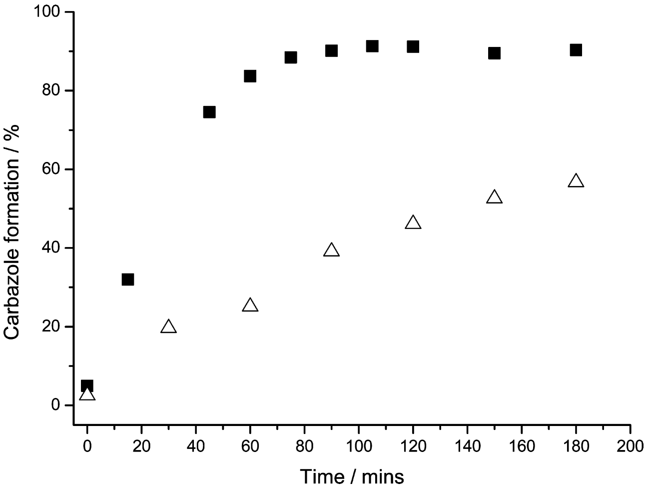


Figure 3. Graph of the formation of CZ with time using fresh powdered catalyst (■) and pellets crushed to less than 75 μm (△). Reaction conditions: in each case, the reaction was carried out over 5 wt % Pd/Al_2O_3 (1 g) with THCZ (2 g) in mesitylene (200 mL) at 135 °C and 4 bar propene.

3.1.3. Catalyst Recycle. For a liquid phase process to be carried out under continuous operation, the catalyst system should be robust for extended periods of time so the reusability of the crushed 5 wt % Pd/Al_2O_3 pellet catalyst was tested using the batch STR. Figure 4 shows that on filtration and rinsing of the catalyst after reaction and its subsequent reuse, the rate of reaction decreased almost 8-fold from 6.94×10^{-5} mol min^{-1} g_{cat}^{-1} to 9.04×10^{-6} mol min^{-1} g_{cat}^{-1}. Washing the catalyst with acetone overnight restored some of the activity with the rate increasing again to 1.87×10^{-5} mol min^{-1} g_{cat}^{-1} and the initial activity being fully obtained after 10 such treatments with acetone. As this method of regenerating the activity of the catalyst is not only time-consuming but also uses a lot of solvent, Soxhlet extraction was used to regenerate the initial activity of a used catalyst and, as shown in Figure 4, the initial activity of the catalyst was regained.

These results indicate that there is a heavy, but acetone soluble byproduct produced, which deactivates the system. Interestingly, the initial rate of reaction was not regained on recalcination of a used catalyst at 500 °C due to either sintering of the palladium particles or more likely formation of more

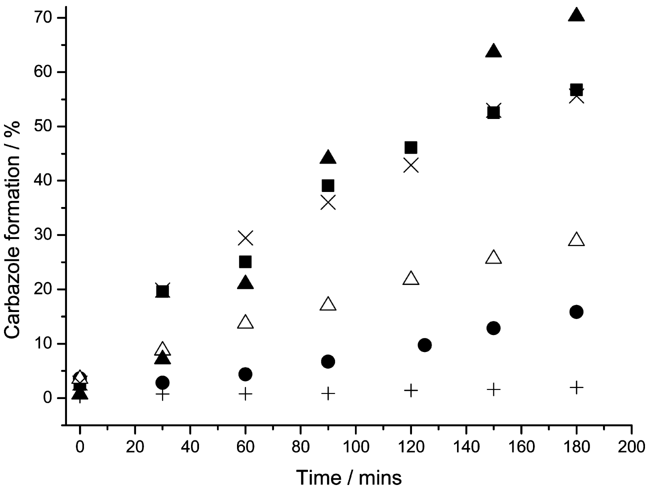


Figure 4. Graph of the formation of CZ with time using fresh crushed catalyst pellet (■) and used catalyst subjected to different regeneration procedures. No wash (●), 12% of initial activity; used catalyst washed with acetone overnight (△), 25% of initial activity; used catalyst washed with acetone for 10 days (×), 100% of initial activity; used catalyst washed with acetone using Soxhlet extraction (▲); and the used catalyst recalcined (+). Reaction conditions: the reactions were carried out over 5 wt % Pd/Al_2O_3 (1 g) with THCZ (2 g) in mesitylene (200 mL) at 135 °C and 4 bar of propene.

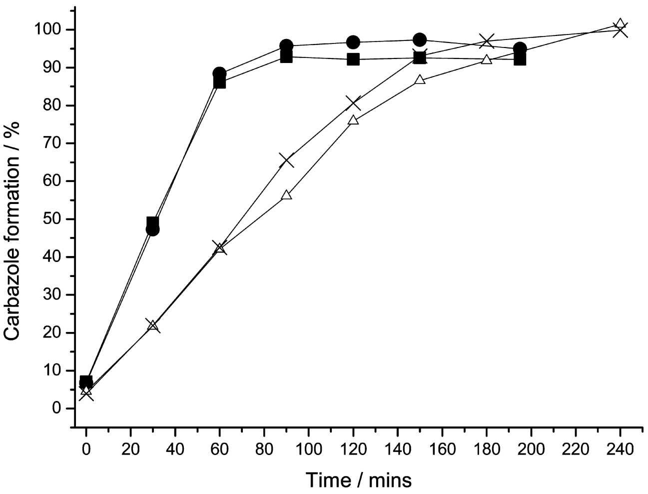


Figure 5. Graph of the formation of CZ with time using fresh 5 wt % Pd/C (■) and used 5 wt % Pd/C catalyst washed with acetone overnight (●) and fresh 5 wt % Pd/α Al_2O_3 (△) and used Pd/alpha Al_2O_3 catalyst washed with acetone overnight (×). Reaction conditions: the reactions were carried out over catalyst (1 g) with THCZ (2 g) in mesitylene (200 mL) at 135 °C and 4 bar propene.

strongly adsorbed coking products, which in turn were more severely deactivating.

It should be noted that the deactivation was more severe when using pellets compared to powder where 43% of the initial activity was retained on the second reuse of the catalyst with no washing (Figure S3 of the Supporting Information). Therefore, the build up of byproducts in the pores of the catalyst caused by poor mass transfer or metal dispersion may play an important role in the production of this poison. Overall, these results show that the catalyst is deactivated by strong adsorption of a poison, formed during reaction, on the catalyst surface and provided the poison can be removed, the activity of the catalyst can be regenerated. A similar observation was made by the group of Libuda during the dehydrogenation of dodecahydro-*N*-ethylcarbazole above 350 K.[14] Strongly bound species were observed on the surface of the catalyst, some of which were identified as dehydrogenation intermediate products or decomposition products whilst others remained unidentified. Attempts were made in this work to isolate and identify the byproduct by Soxhlet extraction of a spent catalyst; however, all efforts to observe material other than those present in the reaction by GC, HPLC, or NMR were unsuccessful. With typical mass balances throughout the reaction being in excess of 95% and no unidentified peaks being observed by GC analysis of the liquid phase, the byproduct formed was considered to be present in small amounts, although strongly adsorbed to the catalyst surface.

3.2. Catalyst Modification. Secondary reactions leading to the formation of an unidentified product may be attributed to active sites on the alumina support itself. This hypothesis was supported by the efficient recycle of 5 wt % Pd/C and 5 wt % Pd/α-Al_2O_3 catalysts (Figure 5). Alpha alumina has been shown to have lower acidity than the gamma form,[22] and this was supported here where the density of acid sites on the alpha alumina catalyst was found to be negligible under pyridine adsorption analysis. However, the commercially available pelletised 5 wt % Pd/Al_2O_3 was most suitable for use in the TBR, so potential methods to modify the commercial catalyst were investigated.

The presence of acidic sites on the commercial alumina were considered to be potential sites for byproduct formation. To remove these active support sites, the commercial 5 wt % Pd/Al_2O_3 catalyst pellets were washed with a range of bases: lithium, sodium, and potassium hydroxide.[23] These treated catalysts, 5 wt % Pd/Al_2O_3(Li, Na, or K), were subsequently used in a standard dehydrogenation reaction, and Figure 6 shows that in all cases, the rate of reaction increased compared to the untreated catalyst from 6.94×10^{-5} mol min^{-1} $g_{cat}{}^{-1}$ using 5 wt % Pd/Al_2O_3 to 1.61×10^{-4} mol min^{-1} $g_{cat}{}^{-1}$ using 5 wt % Pd/Al_2O_3(Na).

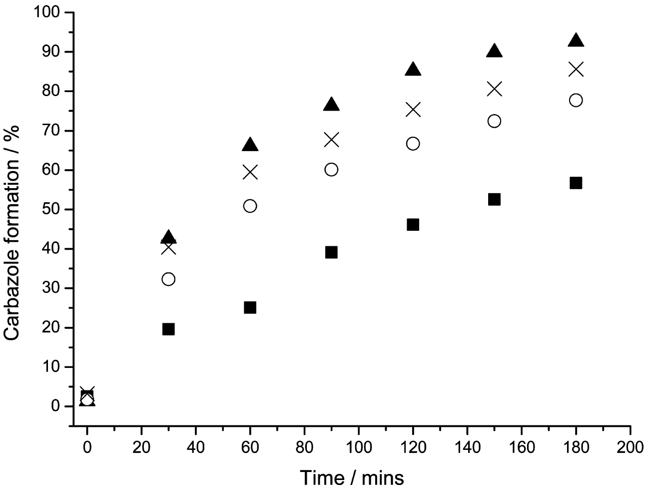


Figure 6. Graph of the formation of CZ with time using freshly crushed pellet catalyst (■) and catalyst washed with different bases: lithium hydroxide, 5 wt % Pd/Al_2O_3(Li) (○), potassium hydroxide 5 wt % Pd/Al_2O_3(K) (×), and sodium hydroxide 5 wt % Pd/Al_2O_3(Na) (▲). Reaction conditions: in each case the reaction was carried out over 5 wt % Pd/Al_2O_3 or 5 wt % Pd/Al_2O_3(Li, Na, or K) (1 g) with THCZ (2 g) in mesitylene (200 mL) at 135 °C and 4 bar of propene.

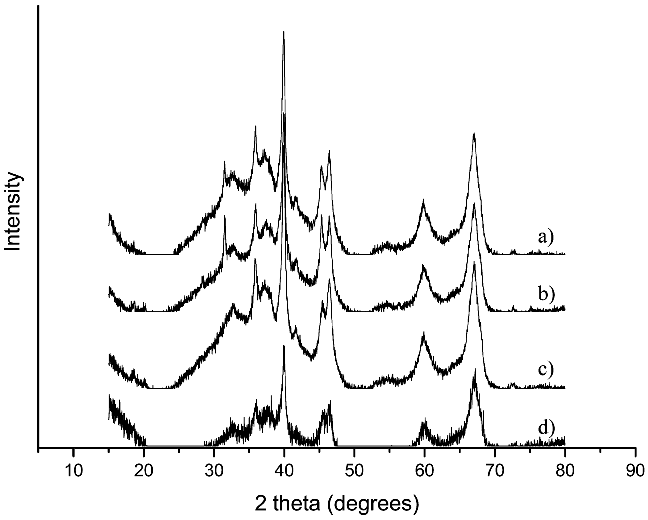


Figure 7. XRD patterns of (a) 5 wt % Pd/Al_2O_3, (b) used 5 wt % Pd/Al_2O_3, (c) 5 wt % Pd/Al_2O_3(Na), and (d) used 5 wt % Pd/Al_2O_3(Na).

Characterisation of 5 wt % Pd/Al_2O_3(Na) by XRD analysis (Figure 7) showed that although the support remained intact after base treatment, some changes did occur with the disappearance of the peak at 2 theta = 31.5 degrees, attributed to theta alumina, after treatment. Identification of the other XRD peaks are given in Table S1 of the Supporting Information and show the presence of gamma, theta, and delta alumina in the support. In addition, the surface area of the catalyst increased after sodium hydroxide treatment (Table 1). The density of acid sites on the catalyst before and after treatment was quantified using pyridine-TPD. The results, summarised in Table S2 of the Supporting Information, show a greater than 20% decrease in acid sites on washing with sodium hydroxide, signifying a decrease in sites that could be responsible for formation of the poison, resulting in a correspondingly faster rate of reaction.

The structure and acidity of alumina is often unclear with electronic and structural properties of the support and metal changing with the extent of hydration, thermal treatments, and exposure to acidic or basic media. Therefore, the decrease in acid sites may be just part of the explanation for the increased rate of reaction observed on the base-washed catalysts. Adsorption of THCZ on palladium is known to occur through the aromatic ring with all intermediates and the carbazole product retaining this interaction throughout the dehydrogenation process.[17b] The presence of an electron donating sodium on the surface of the catalyst may alter the adsorption strength of the organic substrates, intermediates, and products, thereby decreasing the deactivating effect of strongly bound poisoning byproducts. Here, THCZ was taken as a representative model compound present in this reaction and an adsorption isotherm on 5 wt % Pd/Al_2O_3 was compared with that for 5 wt % Pd/Al_2O_3(Na). Figure 8 shows that for concentrations below saturation of the catalyst surface, the concentration of THCZ adsorbed per unit area of catalyst surface is less for the sodium-hydroxide-washed catalyst than the untreated catalyst.

Weaker adsorption of the organic substrate, intermediate, or product will decrease the occurrence of secondary reactions forming the poison and also decrease the adsorption strength of any poison molecules formed.

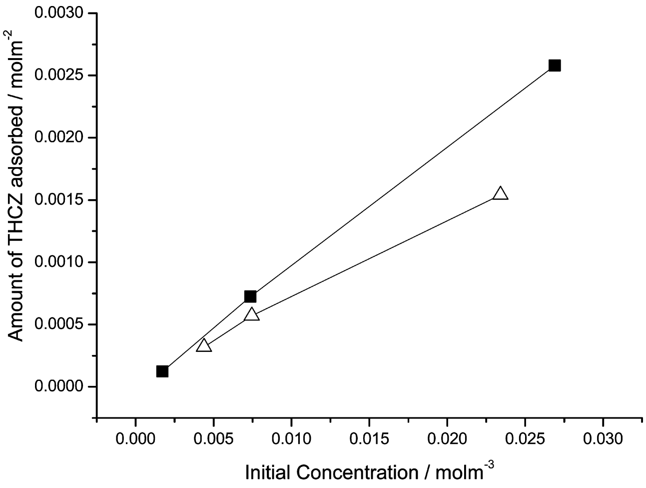


Figure 8. Adsorption isotherms of THCZ adsorbed onto the surface of 5 wt % Pd/Al_2O_3 crushed pellets (■) and onto the surface of 5 wt % Pd/Al_2O_3(Na) (△).

The increase in the rate observed with the base-washed catalysts may be due to the decrease in acid sites resulting in fewer poisons formed on the surface of the catalyst during the reaction, or the presence of sodium reducing the adsorption strength of the organic compounds, or a combination of both of these effects. Although at present the increased rate cannot be attributed to one reason, the kinetic results and characterisation indicate that the nature of the sodium-hydroxide-washed catalyst may be suitably modified to decrease the deactivation and so a recycle study was carried out.

The 5 wt % Pd/Al_2O_3(Na) catalyst was recycled by removing it from the reactor, washing it with acetone, and drying it overnight at 120 °C. Figure 9 shows a progressive decrease in reaction rate on the second and third run; however, the reaction rate of 5 wt % Pd/Al_2O_3(Na) used for the third time was similar to that of 5 wt % Pd/Al_2O_3 used for the second time. There was no change observed in the structure of 5 wt %

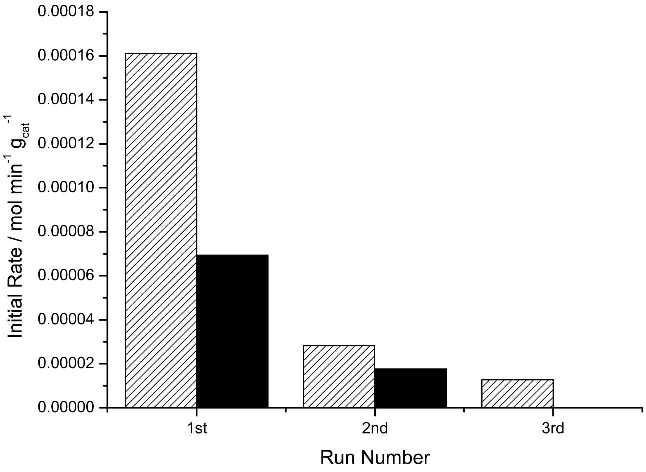


Figure 9. Graph of the initial rate of reaction for the formation of CZ over a number of uses using 5 wt % Pd/Al_2O_3 (blacked out bar) and 5 wt % Pd/Al_2O_3(Na) (striped bar). Reaction conditions: the reactions were carried out over 5 wt % Pd/Al_2O_3 or 5 wt % Pd/Al_2O_3(Na) (1 g) with THCZ (2 g) in mesitylene (200 mL) at 135 °C and 4 bar of propene.

Pd/Al_2O_3 or 5 wt % $Pd/Al_2O_3(Na)$ on recycle, as shown by XRD analysis (Figure 7).

Sodium hydroxide on alumina supports is easily removed in the presence of polar solvents such as acetone,[24] so to overcome the effect of the acetone wash on the sodium-hydroxide-washed catalyst, the recycle experiment was repeated but this time included a secondary washing step with sodium hydroxide after each acetone wash. The results shown in Figure 10 demonstrate that under these conditions the initial activity of the catalyst was retained even after 3 runs. This stabilised catalyst was considered suitable for continuous testing.

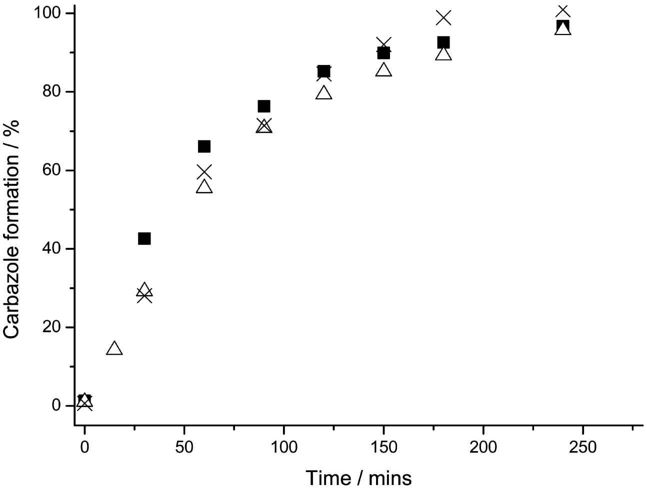


Figure 10. Graph of the formation of CZ with time using sodium-washed catalyst for three uses: first use (■), second use (△), and third use (×). Reaction conditions: the reactions were carried out over 5 wt % $Pd/Al_2O_3(Na)$ (1 g) with THCZ (2 g) in mesitylene (200 mL) at 135 °C and 4 bar of propene. The used catalyst was filtered from the reaction mixture, washed with acetone followed by a secondary washing with sodium hydroxide before being dried, and used in subsequent runs.

3.3. Kinetic Reactions in the Trickle Bed Reactor.

3.3.1. Evaluation of the Trickle Bed Reactor in Semibatch Mode.

To ensure the data obtained in the batch STR could be applied to the reaction carried out continuously, a series of experiments were carried out with the trickle bed reactor operated in the semibatch mode, where the gas was continuously fed through the system and the liquid feed was recycled using the metering pump. Figure 11 shows a typical reaction profile for a semibatch reaction with Figure S4 of the Supporting Information showing that the order changes from zero order to first order after around 7 hours reaction time. The rate of reaction in the trickle bed reactor was over 70 times slower than the STR with the rate in the TBR being 8.3×10^{-7} mol min^{-1} g_{cat}^{-1} compared to 6.94×10^{-5} mol min^{-1} g_{cat}^{-1} obtained when the crushed pellets were tested in the STR. Similarly to the STR, no other products were observed in the TBR (Figure S5 of the Supporting Information).

As was previously reported for the STR,[16] the reaction in the TBR was found to be zero order with respect to propene (Figure S6 of the Supporting Information). It is known that the rate of reaction is strongly dependent on the size of the catalyst particles used and here the use of the 3 mm catalyst pellets required for the fixed bed was expected to result in mass transfer limitations. This was confirmed by running the reaction at different temperatures and using the Arrhenius Equation to obtain the apparent activation energy of the reaction. Figure S7 of the Supporting Information shows that the rate of reaction increases with increasing temperature and that the reaction has an apparent activation energy of 27.2 kJ mol^{-1} under these conditions, significantly lower than 71 kJ mol^{-1} obtained using crushed pellets in a STR.[16] One outcome of the reduced rate of reaction is that the build-up of hydrogen in the pores of the catalyst is less of a problem than in the batch STR studies, meaning the presence of a hydrogen-accepting gas has less of an effect on the rate of reaction. Figure 12 summarises the

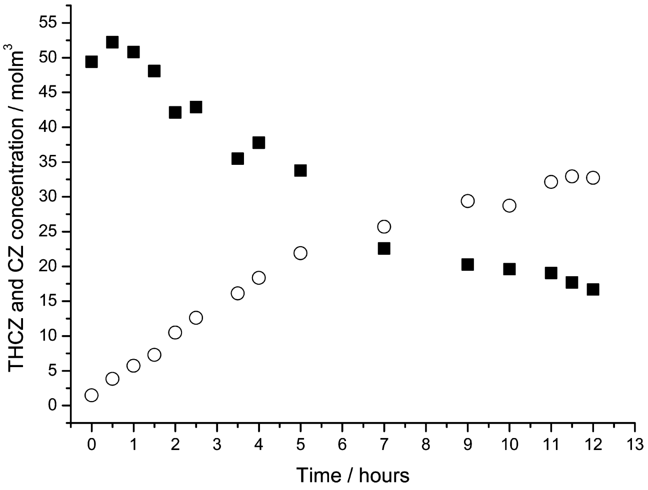


Figure 11. Graph showing the dehydrogenation of THCZ (■) and the formation of CZ (○) with time in the trickle bed reactor operated in the semibatch mode. Reaction conditions: the reaction was carried out over 5 wt % Pd/Al_2O_3 pellets (42 g) with THCZ (4 g) in mesitylene (400 mL) at 150 °C and 1 bar propene, using a liquid flow rate of 167 mL min^{-1} and a gas flow rate of 200 mL min^{-1}.

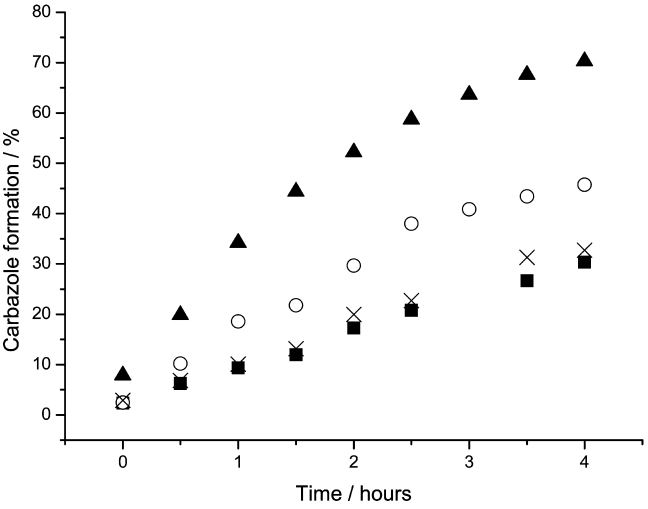


Figure 12. Graph showing the formation of CZ with time in the trickle bed reactor operated in semibatch mode over 5 wt % Pd/Al_2O_3 pellets with an N_2 purge gas (■), 5 wt % Pd/Al_2O_3 pellets with a propene purge gas (×), 5 wt % $Pd/Al_2O_3(Na)$ pellets with an N_2 purge gas (○), and 5 wt % $Pd/Al_2O_3(Na)$ pellets with a propene purge gas (▲). Reaction conditions: in each case, the reaction was carried out over 5 wt % Pd/Al_2O_3 or 5 wt % $Pd/Al_2O_3(Na)$ pellets (43 g) with THCZ (4 g) in mesitylene (400 mL) at 150 °C and 1 bar of propene or N_2, using a liquid flow rate of 167 mL min^{-1} and a gas flow rate of 200 mL min^{-1}.

effect of base washing and propene on the rate of reaction in the TBR. It was previously reported that in the STR, a 5-fold increase in rate could be obtained upon changing from a nitrogen purge to remove the hydrogen to a 5 bar pressure of propene.[16] When the reaction was run in the semibatch TBR system, only a 1.1-fold increase in rate was observed with the rate increasing from 6.45×10^{-7} mol min^{-1} g$_{cat}$$^{-1}$, using 1 bar of nitrogen pressure, to 7.32×10^{-7} mol min^{-1} g$_{cat}$$^{-1}$, using the same pressure of propene. Here the propene is less significant due to the low rate of reaction; the kinetics are controlled to a greater extent by the reaction rather than the transport of hydrogen from the pores.

The batch STR system showed that the sodium hydroxide wash resulted in a 2.3-fold increase in rate, and a similar 1.9-fold increase was observed in the semibatch TBR in the presence of nitrogen. Here the faster rate of reaction causes a build up of hydrogen within the pores of the catalyst, and the kinetics become increasingly controlled by the transport of this hydrogen out of the pores. In this case, the effect of propene was more pronounced with a further 1.8-fold increase in rate observed from 1.20×10^{-6} mol min^{-1} g$_{cat}$$^{-1}$ with nitrogen to 2.17×10^{-6} mol min^{-1} g$_{cat}$$^{-1}$ with propene.

It is clear, therefore, that a comparison of the rate of the untreated catalyst in nitrogen with that observed using a sodium-washed catalyst in the presence of propene should result in the greatest increase in rate, and a 3-fold increase was observed. In summary, the least active system was the untreated catalyst used in the presence of nitrogen and by applying a simple base wash and using a hydrogen acceptor gas, the rate of reaction was increased by over 3-fold.

3.3.2. Continuous Dehydrogenation of THCZ. With the results obtained in the batch STR generally translating to the TBR and the recycle of the base-washed catalyst demonstrated in the batch STR, the reaction was run under continuous operation in the TBR. Here the deactivation of the untreated catalyst and the catalyst washed with sodium hydroxide could be compared. Conditions used for continuous operation were similar to those used for the semibatch experiments with the gas flow at 200 mL min^{-1}, and the liquid flow set to 167 mL min^{-1}. The liquid inlet and outlet were 1 mL min^{-1}, giving a recycle ratio of 99.75%.

Figure 13 shows that, as expected, when using the untreated catalyst, an initially rapid rate of reaction was observed followed by a continuous deactivation, until the reaction ceased after 10 h on stream.

When the sodium-hydroxide-washed catalyst was used in the TBR under continuous operation, again an initially rapid rate of reaction was observed, followed by a slight decrease in conversion to 22 mol m^{-3} (37%) (see Figure 14). However, in this case, the conversion then leveled off to show a region of steady state which lasted for 50 h of reaction time, at which point the reaction was stopped.

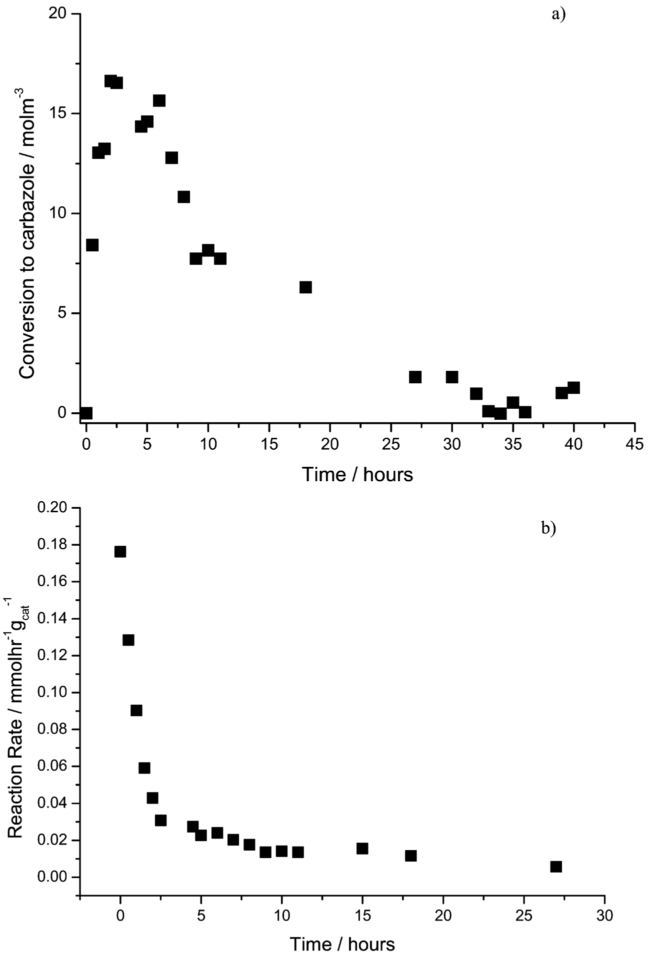


Figure 13. Graph showing (a) the formation of CZ with time in the trickle bed reactor operated in continuous mode using a propene purge over the untreated 5 wt % Pd/Al_2O_3 catalyst and (b) the change in the rate of reaction with time on stream. Reaction conditions: the reaction was carried out over 5 wt % Pd/Al_2O_3 pellets (43 g) with THCZ (4 g) in mesitylene (400 mL) at 150 °C and 3 bar of propene, using a liquid flow rate of 167 mL min^{-1} and a gas flow rate of 200 mL min^{-1}.

4. CONCLUSIONS

The ability of the sodium-hydroxide-washed catalyst to operate under continuous operation demonstrates the viability of continuous dehydrogenation reactions using a TBR. Treatment of the catalyst with sodium hydroxide resulted in a catalyst with increased activity shown by the increased rate of reaction observed in the STR and increased stability shown by the region of steady state observed in the TBR compared to an untreated catalyst. The increased activity has been attributed to a combination of the lower acidity of the support, resulting in fewer byproducts being formed and decreased adsorption strength of organic reagents. In addition, use of a continuous flow reactor has highlighted aspects of deactivation of this catalyst that were not evident using a batch STR. By testing deactivation of the catalyst in the batch STR, the results were influenced by the effects of the regeneration treatments on the catalyst between runs rather than just deactivation occurring during the reaction. It is proposed that a small amount of as-yet unidentified material forms over the untreated catalyst and adsorbs strongly onto the catalyst surface, reducing the rate of reaction and eventually poisoning the catalyst. However, a simple wash with a base is sufficient to modify the catalyst properties in such a way as to increase the rate of reaction and limit formation and adsorption of the poison, allowing the dehydrogenation reaction under continuous operation. Although not the primary motivation for this work, it is noted that the improved rate of reaction and reuse observed with the base-washed catalyst makes this an interesting catalyst for further investigation for a hydrogen storage application.

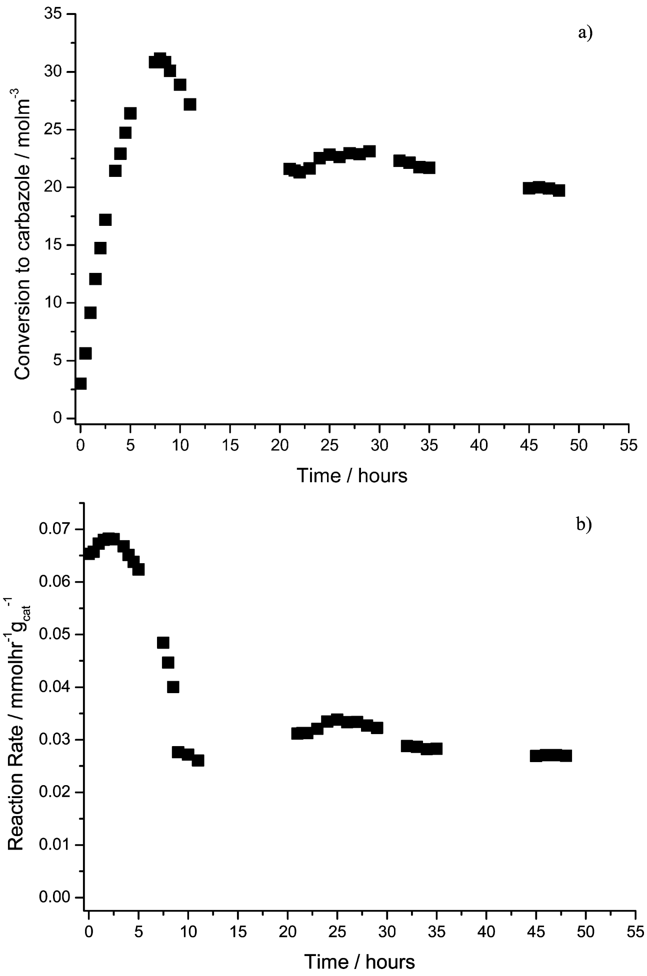


Figure 14. Graph showing (a) the formation of CZ with time in the trickle bed reactor operated in continuous mode, using a propene purge over the sodium-hydroxide-washed 5 wt % Pd/Al_2O_3 catalyst and (b) the change in the rate of reaction with time on stream. Reaction conditions: the reaction was carried out over 5 wt % Pd/Al_2O_3 pellets (43 g) with THCZ (4 g) in mesitylene (400 mL) at 150 °C and 1 bar of propene, using a liquid flow rate of 167 mL min^{-1} and a gas flow rate of 200 mL min^{-1}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Identification of XRD peaks, density of acid sites, figure of fixed catalyst bed, curve fitting of rate equations, graph of CZ formation, graphs of comparison in CZ formation with time. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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