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The conversion of 1,8-cineole sourced from renewable Eucalyptus oil to *p*-cymene over a palladium doped γ-Al_2O_3 catalyst

Benjamin A. Leita[a,*], Peter Gray[b], Mike O'Shea[b], Nick Burke[a], Ken Chiang[a], David Trimm[a]

[a] CSIRO Earth Science and Resource Engineering, Private Bag 10, Clayton South VIC 3169, Australia
[b] CSIRO Materials Science and Engineering, Private Bag 10, Clayton South VIC 3169, Australia

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ABSTRACT

The conversion of 1,8-cineole, sourced from the steam distillation of Eucalyptus waste, to *p*-cymene has been studied. Both alumina and palladium on alumina have been found to be active catalysts, the latter producing *p*-cymene in near quantitative conversion. Catalyst testing coupled with catalyst characterisation showed the catalysts to be multifunctional, promoting dehydration, dehydrogenation and isomerisation in a one step process.

1. Introduction

Para-cresol is an industrially important chemical used in the manufacture of pharmaceuticals, dyes and fertilisers [1]. Cresols are generally produced *via* a two step process, the Friedel–Crafts isopropylation of toluene to give mixed cymene isomers, followed by an oxidation to yield mixed cresols and acetone [2]. Although the raw materials are inexpensive, mixed cresols are produced, which both are challenging to separate and of limited value in that only *p*-cresol has widespread uses.

Alternative synthetic routes based on naturally occurring chemicals such as pinenes, terpenes and cineole have recently found favour [3,4]. In particular, 1,8-cineole hereafter referred to as cineole, isolated by steam distillation of Eucalyptus oil [5–7], has been heated in the presence of supported metal catalysts to produce both terpenes and high yields of *p*-cymene (Scheme 1).

Related reactions have been studied previously [8,9]. Matsuura and Waki [10] found that gamma alumina catalysed the pyrolysis of cineole above about 220 °C, conversion being complete at 300 °C. Alumina was suggested to promote dehydration of cineole to dipentene, some of which then reacted further to cymene. Hügel et al. [11] found that platinum and palladium catalysts supported on silica promoted hydrogenolysis of cineole to *p*-menthanes and, when pumice was used as a support, to *p*-cymene with yields of up to 70%.

Both the metal and the support were suggested to affect the reaction sequence and this was supported by Roberge et al. [12] who studied the conversion of pinenes to *p*-cymene. They found that the supported palladium catalyst displayed dual-functionality, with metal sites responsible for hydrogenation/dehydrogenation and acid sites on the support responsible for isomerisation [13].

Earlier preliminary studies have shown that palladium on alumina was an excellent catalyst for the conversion of cineole to *p*-cymene [3]. The present paper reports more extensive studies of the efficiency and mechanism of the reaction.

2. Experimental

2.1. Catalyst preparation and characterisation

Palladium doped γ-Al_2O_3 catalysts were prepared by wet impregnation. γ-Al_2O_3 pellets (Saint-Gobain NorPro) were first dried at 90 °C and then immersed in an aqueous solution of palladium nitrate dihydrate. The mixture was stirred and the solvent removed (60 °C for 4 h in vacuo). The Pd-γ-Al_2O_3 catalysts were then dried and calcined at 350 °C for 12 h. The total metal content (0.38% Pd on γ-Al_2O_3) was assessed by ICP analysis (Varian Vista ICP-OES). The BET surface area was determined by the adsorption of N_2 (Micromeretics Tristar 3000). Metal surface area determination and temperature programmed reduction experiments were

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[*] Corresponding author. Tel.: +61 3 95458130; fax: +61 3 95458380.
E-mail addresses: benjamin.leita@csiro.au, ben.leita@csiro.au (B.A. Leita).

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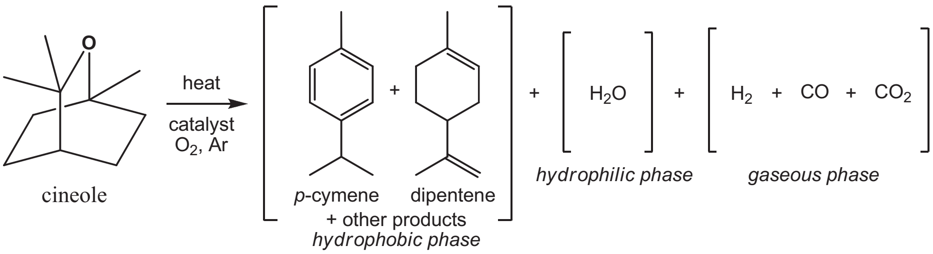


Scheme 1. General scheme for the catalytic transformation of cineole over metal doped γ-Al_2O_3 catalysts [3].

carried out on a Micromeretics AutoChem. Metal surface areas were obtained by hydrogen and carbon monoxide chemisorption, the catalysts being reduced for 4 hr in hydrogen before analysis. Prior to temperature programmed reduction (TPR) the fresh catalyst was dried in argon at 150 °C, cooled to 50 °C and reduced in a stream of 10% H_2 in Ar. The temperature was increased at a rate of 5 °C/min to 600 °C, where it was held for 30 min before cooling to ambient temperature at a rate of 10 °C/min.

2.2. Catalytic activity measurements

All reactions were studied using an electrically heated stainless steel down flow tubular reactor (13.5 mm internal diameter, 300 mm length) maintained at a pre-set temperature and atmospheric pressure. A K-type thermocouple was used to monitor the temperature of the catalyst bed. The liquid product was collected by a two trap trapping system, the first trap at 40 °C collected all the liquid products and the second trap was at 0 °C to insure only the gaseous products went through into an online gas chromatograph for analysis.

In a typical experiment, 3 g of catalyst was loaded into a stainless steel mesh basket and placed inside the tubular reactor. The temperature was stabilised for 1 h before injection of feedstock. Liquid cineole was injected into a stream of carrier gas (150 mL/min) upstream of the pre-heater (200 °C) at a rate of 0.5 mL/min using an ISCO 500D syringe pump. As the reaction started the furnace temperature was adjusted to maintain the desired bed temperature.

Organic and aqueous fractions were collected together from the first trap. The aqueous fraction was found to be predominantly water, with very small traces of cineole *via* GCMS and ^{1}H NMR. The organic/oil product (10 μL) was dissolved in 1.5 mL of 0.1 v/v% mesitylene in acetonitrile prior to analysis. Mesitylene was used as the internal standard.

These samples were analysed by gas chromatography (Varian CP-3800 equipped with a ZB-5 column (30 m × 0.25 mm × 0.25 μm). and a FID detector). The heating rate used was: 60 °C for 2 min, 10 °C/min to 110 °C, 40 °C/min to 250 °C and remaining there for 2 min. Authentic samples of cineole (Aldrich), *p*-cymene (Aldrich) and dipentene (Aldrich) were used to verify the assignment of identified products. The major products of each oil sample, in most cases *p*-cymene, were confirmed using GCMS and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.

Online analyses of gas products were performed using an online Shimadzu GC 8A fitted with a 12 m HAYESEP Q column (Alltech) and a TCD detector.

3. Results and discussion

TPR analysis using a stream of 10% H_2/Ar over the fresh catalyst showed reduction peaks at 189 °C and 387 °C (Fig. 1), the α peak being assigned to the reduction of PdO by H_2 in both cases (Eq. (1)) [14]. The metal surface area is taken per gram of catalyst. Examination of new and used catalysts produced results summarised in Table 1.

$$PdO + H_2 \rightarrow Pd + H_2O \qquad (1)$$

The lower temperature peak corresponded to a hydrogen/palladium ratio of 0.73, in agreement with the results of Bigey et al. [14]. The second reduction (peak β_1) occurred at temperatures above those used for the cineole reaction and probably corresponds to the reduction of Pd(II) centres bound to the alumina. The used catalyst (see below) gave α and β peaks at higher temperatures of 280 °C and 502 °C. This indicates that the catalyst has undergone some changes, possibly structural indicating surface rearrangement and some sintering of the palladium, or more likely deposits of carbonaceous material during use. The reduction in metal surface area of the used catalyst also suggests either some rearrangement of Pd metal clusters, possibly due to sintering, or coverage of metal sites with carbonaceous deposits during the course of the run. While Pd sintering has been reported at temperatures as low as 300 °C [15,16] it is unusual to see sintering of Pd at such low temperatures [17]. It is more likely that the deactivation seen here is due to fouling of the surface of the catalyst.

TGA analysis performed on the fresh and used catalyst clearly showed loss of mass in a dilute oxygen atmosphere for the used samples, suggesting some build-up of material on the catalyst that could be removed with oxidation. Discolouration of the catalyst

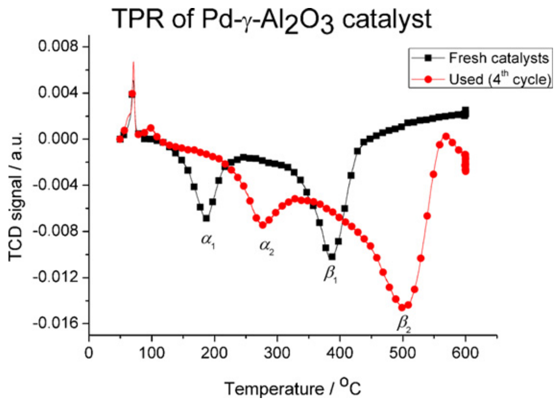


Fig. 1. TPR analysis of the 0.38% Pd-γAl_2O_3 catalyst; Fresh catalyst, 10% H_2 in Ar; temperature increased at a rate of 5 °C/min to 600 °C, and held for 30 min; Used catalyst sample: same conditions.

Table 1
Textural properties of doped γ-Al_2O_3 catalysts.

Catalyst	Specific surface area/m^2 g^{-1}	Metal surface area/m^2 g^{-1}	Pore volume/ cm^3 g^{-1}	Average pore width/Å
Fresh	265	0.906	0.761	115
Used (4th cycle)	220	0.426	0.611	111

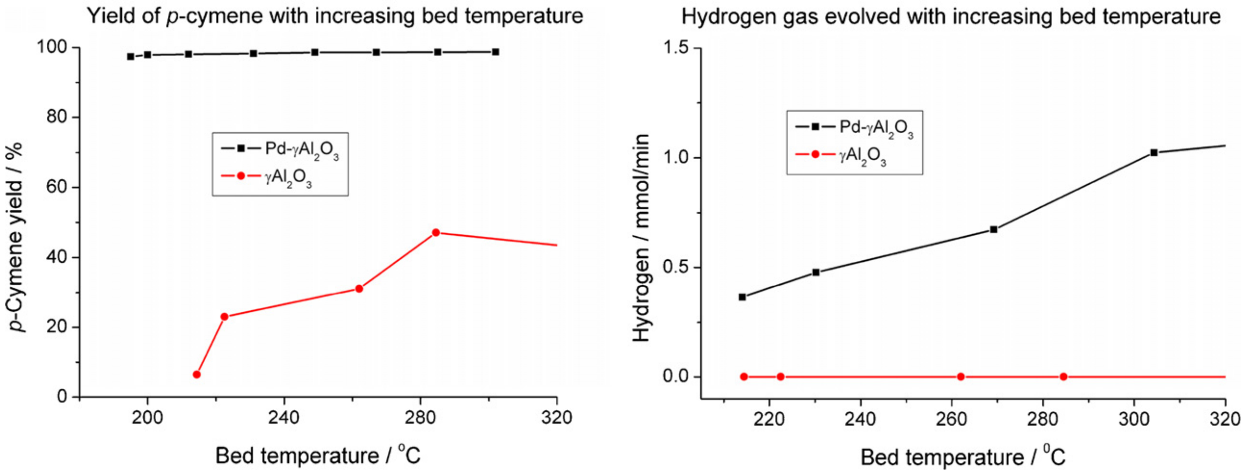
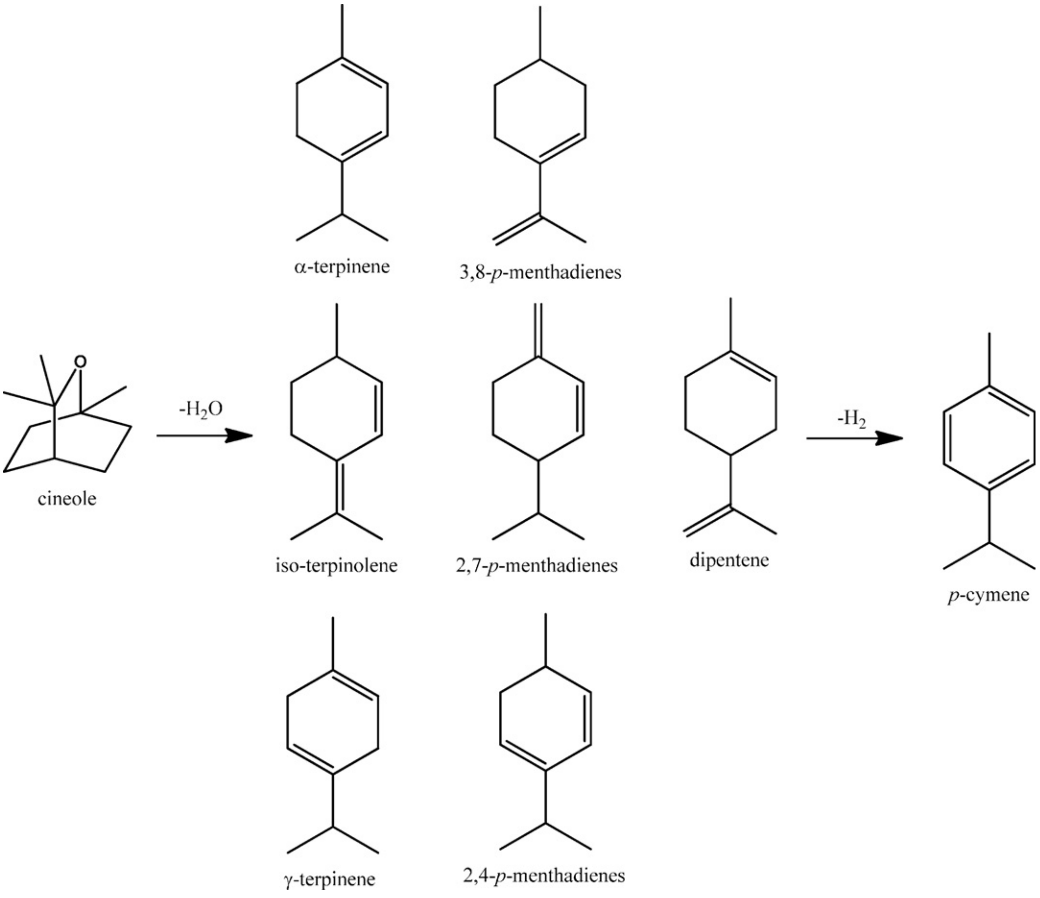


Fig. 2. Product yield as the reaction temperature increased. (γ-Al_2O_3 and 0.38% Pd-γ-Al_2O_3 catalyst, cineole injection 0.5 mL/min, total flow rate of carrier gas 150 mL/min.)

was seen after cycling. This was most obvious at the upstream end of the catalyst bed, suggesting a progressive fouling of the catalyst along the reactor bed. Morra et al. have reported a similar progressive fouling effect in their study on dehydrogenation of *o*-xylene [18]. Attempts to quantify carbon build-up on the catalyst over the course of the reaction were hampered by the heterogeneous nature of the carbon accumulation on the catalyst. In removing the catalyst from the reactor the catalyst did not maintain its orientation as it was in the reactor tube.

Initial screening of catalyst activity was carried out using both the alumina support and the Pd-γAl_2O_3 catalyst. The tests involved a 0.5 mL/min flow of liquid cineole, which was vaporised into a stream of 150 mL/min argon and passed over 3 g of catalyst, which was progressively heated to 350 °C. The observed yield of *p*-cymene and flow rate of hydrogen are summarised in Fig. 2. Both alumina and Pd-γ-Al_2O_3 were found to be catalytically active, conversion of the cineole occurring above ~200 °C. The production of *p*-cymene was lower over alumina with a maximum yield of 47%



Scheme 2. The proposed reaction sequence for the catalytic transformation of cineole into *p*-cymene. The initial reaction involves breakage of the weakest C–O bond in cineole [16] followed by rapid dehydration step followed by a dehydrogenation step to produce a mixture of doubly unsaturated isomers. In the final step, dehydrogenation and rearrangement of the double bonds occurs to produce *p*-cymene.

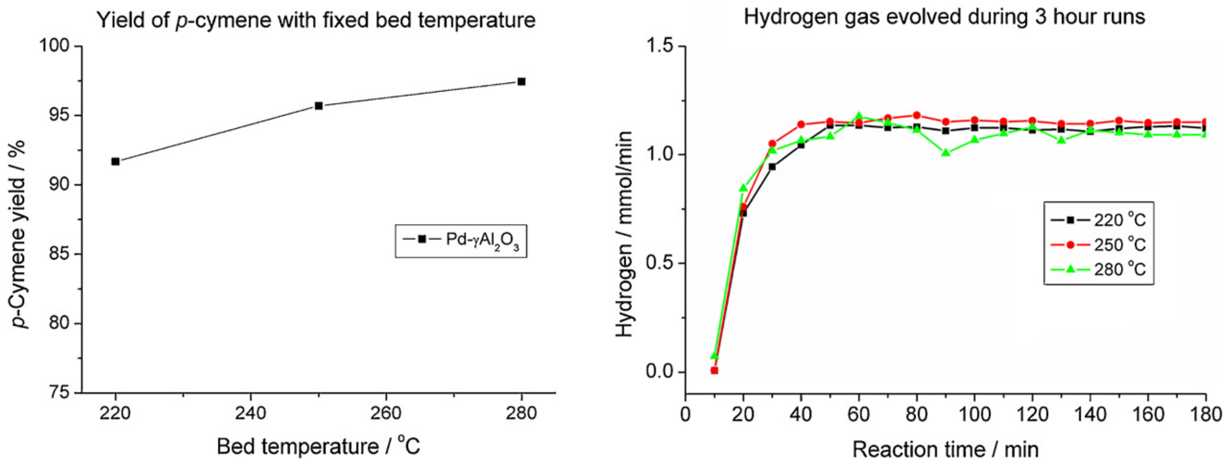


Fig. 3. Product yields over a 3 h time period at fixed reaction bed temperature. Palladium doped γ-Al_2O_3 catalysts, cineole injection 0.3 mL/min, and total flow rate of carrier gas 150 mL/min.

being observed at around 285 °C. No hydrogen was observed until the catalyst was heated to 400 °C. In contrast, *p*-cymene yields were higher over the Pd-γ-Al_2O_3 catalyst but reaction was initiated again at ca 200 °C. Initiation probably resulted from reduction of palladium oxide (189 °C) either by cineole or by hydrogen produced from the alumina catalysed conversion of cineole. The yield of *p*-cymene increased with temperature, reaching a plateau at about 275 °C. Hydrogen yields with Pd-γ-Al_2O_3 catalyst were significantly greater than over alumina alone, reaching a plateau at ca 1.1×10^{-3} mol/min. This is somewhat less than the value of 2.75×10^{-3} mol/(min gcat) expected on the 1:1 stoichiometry of cineole conversion.

It is clear that alumina itself catalyses the conversion of cineole to *p*-cymene, but this was not the case supports such as pumice [11]. Hügel et al. [11] report yields of *p*-cymene increasing from 13% at 200 °C to 68% at 300 °C over the pumice supported palladium system, but the conversion was studied in the presence of 10% hydrogen. The present yields over Pd-γ-Al_2O_3 are significantly higher (ca. 95%), despite the fact that the Pd loading was much lower. Consequently, the high yield observed can in part be attributed to palladium–alumina interactions, not just the additive effect of the palladium and alumina components.

The absence of hydrogen from the alumina results was surprising, particularly in view of the high (47%) conversions that could be achieved. Part of the hydrogen can be expected to reduce PdO in the original catalyst but this should be minimal in a flow system. What seems more likely is that hydrogen is used to gasify carbonaceous deposits. The reaction proceeds *via* dehydration, dehydrogenation and isomerisation with both dehydration and isomerisation being favoured by acidic catalysts, such as alumina [19] (see Scheme 2). Such catalysts are prone to deactivation by deposition of carbonaceous material on the surface [19] which can be minimised by gasification. On the assumption that the difference between expected and observed hydrogen yields over Pd-γ-Al_2O_3 is also due to removal of hydrogen by gasification, the smaller amounts of hydrogen expected to be produced in conversion over alumina would be totally consumed in the same way. At higher temperatures deposition would become faster and the catalytic activity of alumina would decrease, as observed, while the Pd can be expected to catalyse gasification and hence to retain overall catalytic activity.

The conversion sequence suggested by Hügel et al. [11] is similar to what is proposed in Scheme 2. Acid catalysed ring opening of the C–O bond leads *p*-menthen-8-ol which subsequently dehydrates to form a di-olefin. Subsequent rearrangement/dehydrogenation leads to a range of terpenes and to *p*-cymene, and Roberge et al. [12] have shown that the balance between acid catalysis and hydrogenolysis, as controlled by the catalytic components, dictates the final product distribution. Using the conversion of pinenes as

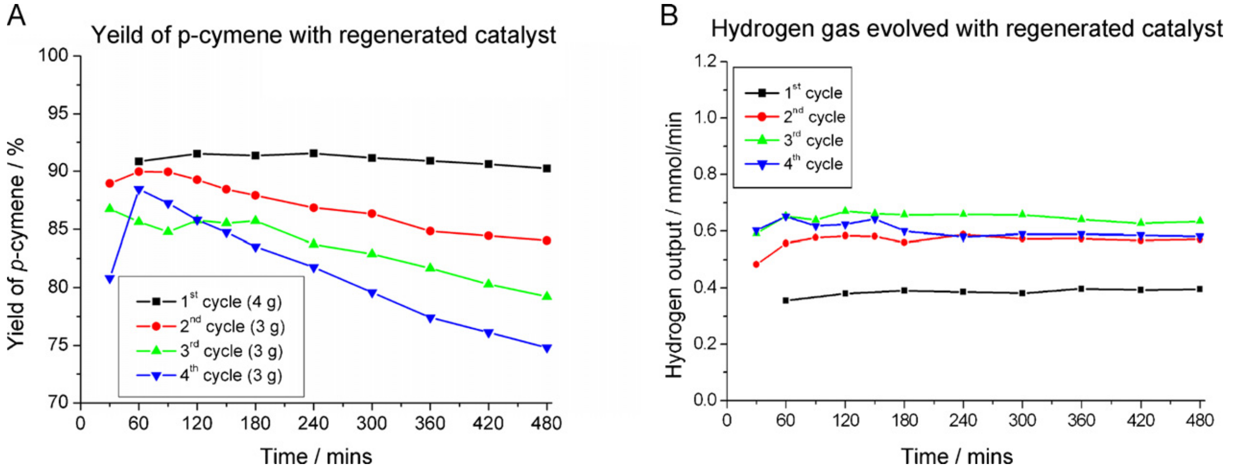


Fig. 4. (A) Left graph shows yields of *p*-cymene as a function of time. (B) Right graph shows hydrogen production over time (8 h run, sample were taken every hour, fixed bed temperature of 250 °C, injection rate for 1,8-cineole of 0.3 mL/min, 4 g (3 g for re-generated) catalyst, 150 mL/min carrier gas, 7.3% oxygen.) (First cycle was carried out with fresh catalyst; subsequent cycles were carried out under the same conditions but after calcinations at 350 °C for 12 h).

an example, Pd-γ-Al_2O_3 was found to be very efficient at producing *p*-cymene.

Roberge et al. also noted catalytic deactivation in the systems [12] and, to investigate this, a further series of experiments was carried out better to quantify the yields of *p*-cymene and hydrogen over the present catalyst at reaction conditions below 300 °C. A series of 3 h runs at fixed bed temperatures of 220, 250 and 280 °C were chosen. The production of hydrogen was monitored continuously against time (Fig. 3) while the liquid phase was collected as one sample over the 3 h period to enable an accurate mass balance of the product.

The liquid phase analysis showed distinct increases in the initial yield of *p*-cymene as the temperature was raised from 220 °C to 250 °C, but little deactivation. A gradual decrease in *p*-cymene with time online was noted and an increase in other terpenes occurred at temperatures greater than ~250 °C. Only very small changes in the amount of hydrogen produced were observed, consistent with the suggestion that the reaction runs at equilibrium.

Although was apparent that the conversion was very stable, longer term deactivation would not be unexpected [12]. As a result, a series of experiments was run in which the effect of regeneration could be studied. Small amounts of oxygen were added to the inlet gas and, after 6 h operation, the catalyst was “regenerated” by calcination at 350 °C for 12 h and the cycle repeated.

The results, shown in Fig. 4, showed a small decrease in *p*-cymene production in the first cycle and a very small deactivation with time online together with, not surprisingly, a larger decrease in hydrogen. Subsequent cycles led to lower yields and to more rapid deactivation (Fig. 4). Part of the deactivation was due to the reduction of metal surface area from $0.906\,m^2\,g^{-1}$ to $0.426\,m^2\,g^{-1}$ in the used catalyst after all 4 cycles. However TPR analysis showed the used catalyst to be fully reduced only at ca 275 °C, a temperature higher than that used for activity testing. Thus, under process conditions, most of the palladium would be present as the catalytically inactive oxide and the bulk of the conversion would result from the activity of the alumina support. More extensive deactivation, as observed, would not be unexpected.

It is clear that Pd-γ-Al_2O_3 is an active and selective catalyst that deactivates very slowly. Regeneration, when it is necessary, must ensure removal of carbonaceous deposit and subsequent reduction to the active palladium metal.

4. Conclusions

The conversion of the bio-renewable feedstock, 1,8-cineole, over a palladium doped γ-Al_2O_3 catalyst is found to produce *p*-cymene as the major hydrophilic liquid product and hydrogen as the major gas products. Both palladium and γ-Al_2O_3 were found to be bifunctional catalysts but the palladium doped system showed very high activity and selectivity, yielding >99% *p*-cymene, while producing large amounts of hydrogen at a bed temperature of ~250 °C. The reaction mechanism is suggested to involve C–O bond fission in cineole, followed by dehydrogenation/isomerisation to produce *p*-cymene. The catalyst was found to be very stable but the possibility of slow deactivation and regeneration was explored. Sequential regeneration led to some loss of activity. The relatively low reaction temperatures, high yields, high selectivity, and minimum waste products of the process make it an attractive route from bio renewable materials to *p*-cymene.

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