Catalysis Today 160 (2011) 50–54

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Reprint of: Oxidative dehydrogenation of cyclohexane and cyclohexene over supported gold, –palladium catalysts[☆]

Nicholas F. Dummer, Salem Bawaked, James Hayward, Robert Jenkins, Graham J. Hutchings[*]

Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, UK

ARTICLE INFO

Article history:
Available online 24 December 2010

Keywords:
Oxidative dehydrogenation
Gold catalysis
Gold–palladium nanoparticles

ABSTRACT

Supported gold, palladium and gold–palladium catalysts have been used to oxidatively dehydrogenate cyclohexane and cyclohexenes to their aromatic counterpart. The supported metal nanoparticles decreased the activation temperature of the dehydrogenation reaction. We found that the order of reactivity was Pd ≥ Au–Pd > Au supported on TiO_2. Attempts were made to lower the reaction temperature whilst retaining high selectivity. The space-time yield of benzene from cyclohexane at 473 K was determined to be 53.7 mol/kg_{cat}/h rising to 87.3 mol/kg_{cat}/h at 673 K for the Pd catalyst. Increasing the temperature in this case improved conversion at a detriment to the benzene selectivity. Oxidative dehydrogenation of cyclohexene over AuPd/TiO_2 or Pd/TiO_2 catalysts was found to be very effective (conversion >99% at 423 K). These results indicate that the first step in the reaction sequence of cyclohexane to cyclohexene is the slowest step. These initial results suggest that in a fixed-bed reactor the oxidative dehydrogenation in the presence of oxygen, palladium and gold–palladium catalysts are readily able to surpass current literature examples and with further modification should yield even higher performance.

1. Introduction

Dehydrogenation of hydrocarbons is carried out on a large scale by the chemical industry. The reaction is central to the activation of alkanes, which are often by-products from petrochemical operations and their conversion, typically to alkenes, provides more reactive intermediates for the production of valuable chemicals for polymers, synthetic rubber and resins [1–3]. Some processes operate in the absence of oxygen but these tend to require very high temperatures. Catalytic oxidative dehydrogenation where the oxygen facilitates the removal of protons, in the presence of a catalyst offers significant advantages over processes in the absence of oxygen since they can operate under more energy efficient conditions, and in the presence of O_2 catalyst deactivation by coke formation is alleviated and thermodynamic constraints are removed. However, the thermodynamically more favourable route to CO_2 formation can be favoured and hence catalyst design focuses on the identification of catalysts that can operate with O_2 at low temperatures thereby limiting CO_2 formation. Consequently catalyst design for oxidative hydrogenation of alkanes is receiving considerable attention at present. Several processes have been commercialised, these include UOP-designed butene production (1940s), the Houdry process (1940s) for butadienes and the Catofin^{TM} process (1980s) for iso-butylene and propylene. Indeed in 2000 ca. 7 million tonnes per annum of C_3–C_4 compounds were produced *via* catalytic oxidative hydrogenation [1–3].

Cyclohexane is produced on a large scale *via* hydrogenation of benzene, it can then be used in a number of further reactions, most notably oxidation to adipic acid a central intermediate in the production of nylon. Dehydrogenation to cyclohexene can additionally be used to form a starting material for adipic acid production [4]. Consequently, it is unusual to consider cyclohexane dehydrogenation as a reaction that is required industrially. This is, however, not the case. Worldwide benzene production stands at around 20 M tonnes per annum, the vast majority of this comes *via* hydrocarbon reforming. During benzene production and its subsequent separation from the 'heart-cut' tower [5] significant quantities of impurities persist; among them cyclohexane and cyclohexene. Removal of these impurities can be demanding and requires high temperatures and it is essential that a more effective lower temperature selective process is designed. We consider that catalytic cyclohexene and cyclohexane oxidative dehydrogenation can provide the answer.

Production of aromatics from cyclic feedstocks such as cyclohexane typically occurs above 600 K at the gas–solid interface [6]. This is typical for supported vanadium oxide, metal phosphates and zeolites (ZSM-5 and Co-ZSM-5). However, for conversions above 20% of cyclohexane temperatures in excess of ca. 800 K are required.

DOI of original article: 10.1016/j.cattod.2010.03.031.

[☆] A publishers' error resulted in this article appearing in the wrong issue. The article is reprinted here for the reader's convenience and for the continuity of the special issue.

[*] Corresponding author.
E-mail addresses: hutch@cardiff.ac.uk, hutch@cf.ac.uk (G.J. Hutchings).

0920-5861/$ – see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.cattod.2010.12.014

Over a range of chromium MCM-41 materials low conversion of cyclohexane (ca. 4%) and selectivities to benzene (20–40%) were reported at 573 K [7]. It is therefore apparent that catalysts typically displaying activity for oxidation reactions require excessive temperatures to achieve appreciable conversions with cyclohexane and consequently CO_2 formation becomes dominant. If this problem of purification is to be solved in an energy efficient manner it is important that improved catalysts are designed.

Recently, Oyama and co-workers [8] showed that supported gold catalysts, and Au/TiO_2 in particular, could be used for oxidative hydrogenation of propane. This was used to provide propene which subsequently could be epoxidised. They, therefore, used a combination of different supported gold catalyst in series; firstly; Au/TiO_2 followed by Au/TS-1. Interestingly, it was reported that the oxidative dehydrogenation of propane was able to occur at temperatures <473 K with these gold-based catalysts and that zeolites, titania, MgO and Ni/Mo catalysts all required higher temperatures [8]. This is not the first report for the potential of gold as a dehydrogenation catalyst, since two earlier studies over 40 years ago alluded to this possibility. Gold was reported to dehydrogenate cyclohexene by Erkelens et al. [9] in 1963 with gold films, and Chambers and Boudart [10] demonstrated the reaction with gold powder in the 1966. The intended target reaction in these two studies was the hydrogenation to cyclohexane, however, benzene was observed. The amount of benzene was found to increase with increasing temperature and decreasing hydrogen pressure. Hence, it is apparent that gold could act as a dehydrogenation catalyst. Selective dehydrogenation of cyclohexene has been reported by Borade et al. [11] with Pd-exchanged α-zirconium phosphate. They report a conversion of ca. 85% with a benzene selectivity of ca. 80% at 473 K in the absence of oxygen. However, cyclohexane was found to be secondary product. In addition, palladium based membranes have recently been used in the production of hydrogen from the dehydrogenation of cyclohexane [12,13].

Significant work by Goodman and co-workers concerning Au–Pd supported catalysts for vinyl acetate formation have attempted to elucidate the effect of Au addition to Pd [14,15]. They report that ensembles of Au–Pd are crucial for activity and selectivity to the acetate. In this case the separation of Pd atoms on the surface of the supported particle into monomeric units improves catalytic performance. Additionally, Au is considered to decrease product decomposition and the formation of carbonaceous deposits.

In this paper we report our initial results for the use supported gold and palladium catalysts to lower the temperature of oxidative hydrogenation of cyclohexane and retain selectivity to benzene. We have used the observations of Oyama and co-workers [8] as a starting point. In previous studies we have shown that alloying gold with palladium can lead to significantly enhanced reactivity for selective redox reactions, in particular alcohol oxidation [16] and the direct synthesis of hydrogen peroxide [17,18]. In this paper we show that $AuPd/TiO_2$ is a highly effective catalyst for cyclohexane oxidative hydrogenation to give benzene at low reaction temperatures. However, the Pd/TiO_2 catalyst demonstrates greater activity. The catalyst shows selectivity in the presence of benzene and so can be considered a potential candidate for the oxidative hydrogenation of cyclohexane and structurally related impurities in the commercial production of benzene.

2. Experimental

2.1. Catalyst preparation

5 wt% Pd, 5 wt% Au and a range of Au–Pd catalysts were prepared by impregnation of TiO_2 (Degussa P25, mainly anatase) *via* an incipient wetness method using aqueous solutions of $PdCl_2$ (Johnson Matthey) and/or $HAuCl_4{\cdot}3H_2O$ (Johnson Matthey). For the 2.5 wt% Au–2.5 wt% Pd/TiO_2 catalyst the detailed procedure used was as described below. An aqueous solution of $HAuCl_4{\cdot}3H_2O$ (10 ml, 5 g dissolved in water (250 ml)) and an aqueous solution of $PdCl_2$ (4.15 ml, 1 g in water (25 ml)) were simultaneously added to TiO_2 (3.8 g). The paste formed was ground and dried at 353 K for 16 h and calcined in static air, typically at 673 K for 3 h.

Two other catalysts were also used for comparison. 5 wt% CuO/Al_2O_3 was prepared by impregnation method with $Cu(NO_3)_2{\cdot}3H_2O$ at the desired concentrations. γ-Al_2O_3 (Purlox 200 m^2/g) was used as the support. The sample was dried at 383 K (24 h) and calcined at 673 K (4 h). $(VO)_2P_2O_7$ coated with silica was a commercial sample supplied by DuPont and has been previously described and characterised extensively [19].

2.2. Catalyst testing

Reactions were conducted in a glass flow micro-reactor (i.d. 3 mm). The reactor temperature was varied and monitored by a thermocouple located inside the micro-reactor. Catalyst samples (0.05 g) were pre-conditioned in a He flow (50 ml/min at atmospheric pressure) for 10 min. Followed by a 20% O_2/He flow (50 ml/min). Reactant (5 ml) was then injected (@ 1.05 ml/h) into a pre-heater to vaporise (250 °C) and mix with the incoming gas stream to direct the vapour to the catalyst. Cyclohexane (Chromosolv, $\geq$99.7%, Riedel de Haën), cyclohexene (purum, $\geq$99.0%, Aldrich) and methylcyclohexene (97%, Aldrich) were used as received. Analysis was conducted with online Varian 3400 GC fitted with FID and DB-Wax capillary column and offline gas samples with a Varian 3800 GC fitted with TCD and FID detectors. Product identification was carried out with a Waters GCT premier GC/MS system fitted with an Agilent HP 5MS capillary column operating in electron ionisation mode.

3. Results and discussion

Our initial experiments were conducted using TiO_2, 5% Au/TiO_2, 5% Pd/TiO_2 and 2.5% Au–2.5% Pd/TiO_2 catalysts with cyclohexene and 1-methylcyclohexene as feedstocks. These catalysts were selected as they have been fully characterised in our previous studies [16–18,20]. The catalysts comprise dispersions of nanoparticles in the size range 2–50 nm with most particles in the 8–10 nm particle diameter range for the 5% Au/TiO_2 and 2.5% Au–2.5% Pd/TiO_2 catalysts. In addition, the 2.5% Au–2.5% Pd/TiO_2 catalysts were alloys and all the Pd and Au were present together in the same nanoparticles which have a pronounced core shell structure with a palladium-rich shell and a gold rich core. Cyclohexene was reacted with oxygen in the flow reactor and the results are shown in Table 1. TiO_2 was found to be reactive at temperatures as low as 423 K. This is consistent with the earlier study by Oyama and co-workers [8] where TiO_2 was shown to be poorly active at 550 K for propane oxidative dehydrogenation to propene and temperatures of over 800 K were required to observe high rates of reaction. As the temperature increases so does the activity of TiO_2 but the selectivity to benzene decreases markedly. Au/TiO_2 was significantly more active, although as the conversion approached 100% the selectivity to benzene decreased and CO_2 was formed. Addition of Pd increased the activity and the selectivity of the catalyst significantly and >99% benzene selectivity could be achieved with 100% conversion at 423 K. However, the use of the supported Pd catalyst exhibited similar levels of activity, although with slightly reduced benzene selectivity. The secondary product in this case was not only CO_2, but also a single oxygen containing hydrocarbon. This minor product was in trace amounts and at present we

Table 1
Conversion of cyclohexene (C) and benzene selectivity (S) of over different catalysts.[a].

Temperature (K)	TiO$_2$		5% Au/TiO$_2$		5% Pd/TiO$_2$		2.5% Au2.5% Pd/TiO$_2$	
	C (%)	S^b (%)	C (%)	S^b (%)	C (%)	S^b (%)	C (%)	S^b (%)
423	11.9	95.1	98.3	97.0	100	97.2	100	>99
473	29.1	84.5	100	86.8	100	91.8	100	82.7
573	36.4	60.5	–	–	–	–	–	–

[a] Conditions: catalyst (0.05 g), 20% O_2/He (50 ml/min), cyclohexene (1.05 ml/h).
[b] Selectivity to benzene.

Table 2
Conversion and toluene selectivity of ODH of methyl cyclohexene over different catalysts.[a].

Temperature (K)	TiO$_2$		5% Au/TiO$_2$		2.5 wt% Au 2.5 wt% Pd/TiO$_2$	
	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
473	0	0	0	0	71.1	60.9
513	0	0	14.7	84.1	95.5	40.6
543	0.6	>99	39.7	64.2	–	–
573	8.3	79.2	68.6	51.9	–	–
613	18.1	56.7	93.2	35.2	–	–
623	34.4	30.0	–	–	–	–

[a] Conditions: catalyst (0.05 g), 20% O_2/He (50 ml/min), methyl cyclohexene (1.05 ml/h).

have been unable to identify it conclusively. For both the Pd and Au–Pd catalysts the space-time yield (STY) of benzene was found to be 229 and 235 mol/kg$_{cat}$/h, respectively. In addition, cyclohexene oxidative dehydrogenation over these catalysts was far more effective than had been previously observed for propane oxidative hydrogenation where only 5% conversion and 70% propene selectivity were observed at 443 K [8]. In view of the high reactivity of cyclohexene we investigated the reactivity of 1-methyl cyclohexene and he results are shown in Table 2. Introduction of a methyl group substituent on the alkene functionality decreased the reactivity substantially; however the marked enhancement in the reactivity of the Au/TiO$_2$ catalyst on introduction of the Pd is readily observed. However, with 1-methyl cyclohexene the selectivity was lower, although toluene was the preferred product. At high temperatures and conversions benzaldehyde was observed as a minor product indicating that toluene, formed during this reaction, underwent subsequent oxidation. The selectivity to benzaldehyde over Au/TiO$_2$ at 613 K was found to be 8.8%, whereas, over the AuPd alloy catalyst this was 41% at 513 K, with CO_2 as the remainder.

In a previous study using lower temperatures with liquid phase reactants we have shown that cyclohexene can be epoxidised by supported Au catalysts [21,22]. In these previous studies we observe no oxidative dehydrogenation, and the epoxide is formed in high selectivities and so clearly epoxidation and oxygen insertion is favoured under the mild liquid phase conditions. Cyclohexane oxidation in the liquid phase with supported Au catalysts also favours oxygen insertion reactions with cyclohexanol and cyclohexanone being formed [23]. The low temperature liquid phase oxidations of cyclohexane and cyclohexene are considered to involve radical pathways. It is therefore of great interest that at much higher temperatures oxidative dehydrogenation is preferred over oxygen insertion as under the reaction conditions in the flow reactor with dilute cyclohexene the relative surface concentration of oxygen will be higher and hence oxygen insertion might have become dominant. The higher temperature must lead to the formation of an oxygen species that favours reaction at hydrogen rather than carbon centres, thereby leading to the enhanced activity for selective benzene formation rather than CO_2.

As the Pd/TiO$_2$ and AuPd/TiO$_2$ catalysts showed high activity and specificity for benzene formation from cyclohexene we used this catalyst for the reaction of cyclohexane. The results are shown in Figs. 1 and 2 and Table 3. The STY of benzene at 473 K over the

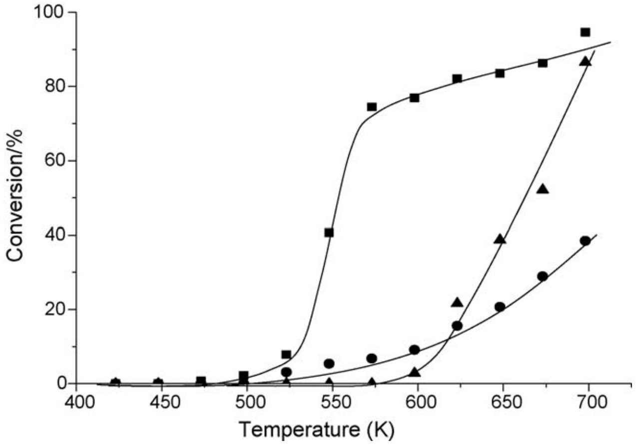


Fig. 1. Cyclohexane conversion over different catalysts; ■ = 2.5 wt% Au 2.5 wt% Pd/TiO$_2$, ▲ = V-P-O silica (DuPont) and ● = CuO/Al$_2$O$_3$.

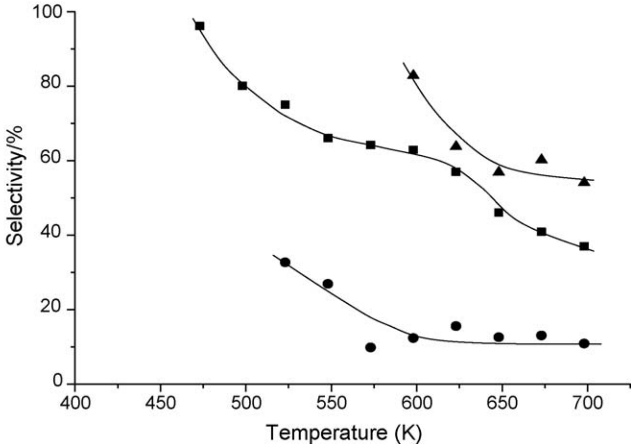


Fig. 2. Cyclohexane ODH selectivity to benzene over different catalysts; ■ = 2.5 wt% Au 2.5 wt% Pd/TiO$_2$, ▲ = V-P-O silica (DuPont) and ● = CuO/Al$_2$O$_3$.

Table 3
Conversion of cyclohexane (C) and benzene selectivity (S) of over different catalysts.[a].

Temperature (K)	TiO_2		5% Au/TiO_2		5% Pd/TiO_2		2.5% Au2.5% Pd/TiO_2	
	C (%)	S^b (%)	C (%)	S^b (%)	C (%)	S^b (%)	C (%)	S^b (%)
473	0	0	0	0	28.1	98.3	0.7	96.1
573	4.8	89.6	32.6	86.6	58.2	72.5	74.5	64.2
673	20.3	52.9	68.2	50.1	86.5	51.9	86.3	40.9

[a] Conditions: catalyst (0.05 g), 20% O_2/He (50 ml/min), cyclohexane (1.05 ml/h).
[b] Selectivity to benzene, remainder CO_2.

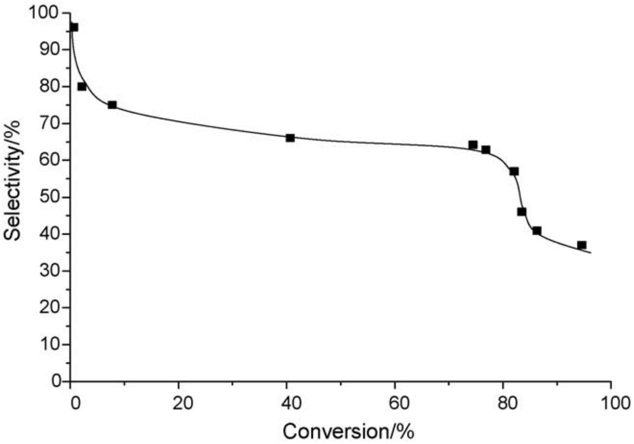
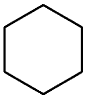
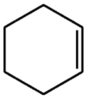
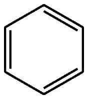


Fig. 3. Cyclohexane conversion versus selectivity to benzene over 2.5 wt% Au 2.5 wt% Pd/TiO_2 catalyst at different temperatures.

Table 4
Percentage remaining of cyclohexane, cyclohexene and benzene over AuPd alloy catalyst at different temperatures.[a].

Temperature (K)	2.5 wt% Au 2.5 wt% Pd/TiO_2		
	 (%)	 (%)	 (%)
473	98.1	0	136
573	21.6	0	129

[a] Conditions: catalyst (0.05 g), 20% O_2/He (50 ml/min), equimolar ratio of cyclohexane, cyclohexene and benzene (1.05 ml/h). Amounts in excess of 100% indicate the net formation of that molecule, amounts lower than 100% indicate the net conversion of that molecule.

Pd/TiO_2 catalyst is 53.7 mol/kg_{cat}/h. At 673 K this yield was determined to be 20.9, 66.4, 87.3, 68.6 mol/kg_{cat}/h for the TiO_2, Au/TiO_2, Pd/TiO_2 and Au–Pd/TiO_2 catalysts, respectively. Comparison with the vanadium phosphate and supported copper oxide catalysts, which are known to possess high oxidation activity, confirms that the $AuPd/TiO_2$ catalyst has both high activity (Fig. 1) and selectivity (Fig. 2). However, cyclohexane is appreciably less reactive than cyclohexene and 1-methyl cyclohexene and much higher reaction temperatures are required. Consequently, the selectivity to benzene decreases as the temperature increases, and this becomes very marked at conversions over 80% (Table 3). This is not observed with cyclohexene conversion. The results suggest a two stage process and Fig. 3 shows the data for benzene selectivity as the conversion increases, although it should be noted these data are not obtained under isothermal conditions. Cyclohexane is initially oxidatively dehydrogenated to benzene we consider *via* initial cyclohexene formation possibly as a transient surface intermediate. The selectivity to benzene approaches 100% at low conversions indicating that the primary reaction pathway is oxidative dehydrogenation and that CO_2 is formed by a sequential process. As benzene shows high stability to oxidation in the lower temperature range we consider that the CO_2 formation probably arises from competing oxygen insertion reactions with surface intermediates, but at this stage we have not carried out detailed mechanistic studies. At conversions above 80%, which for cyclohexane require high temperature (Fig. 1), the oxidation of benzene starts to become favoured.

In a final set of experiments we co-fed equimolar amounts of cyclohexane, cyclohexene and benzene over the $AuPd/TiO_2$ catalyst and the results are shown in Table 4. This is therefore a competitive experiment where the relative reactivities of the reactant, intermediate and product can be studied. As expected, all the cyclohexene is converted selectively to benzene and only partial conversion of the cyclohexane is observed, while at the two temperatures investigated benzene was not stable towards subsequent oxidation; since the amount produced is significantly less than the cyclohexene and cyclohexane converted. In contrast when benzene was passed over the Au–Pd catalyst with 20% O_2/He at 473 and 573 K there was a net loss to CO_2 of 8 and 14%, respectively. Therefore, we consider that the increased instability of benzene in the co-fed experiments is due to the reaction of one species setting up reactive intermediates that facilitate the oxidation of the second component presumably by making a reactive radical species with O_2.

It is interesting to note that the addition of gold to palladium does not lead to enhancement in activity in this oxidative dehydrogenation reaction. This is in contrast to the significant synergistic enhancement in activity we observe for the addition of gold to palladium for alcohol oxidation [16] or the direct synthesis of hydrogen peroxide [18]. In this case we consider that the first step involves dehydrogenation and palladium is able to activate this initial step more facilely due to the solubility of hydrogen in palladium. As gold forms core shell alloys with palladium using the preparation method we have used [16], with a palladium-rich shell, the added gold serves as a diluent within the alloy nanoparticles.

4. Conclusions

Oxidative dehydrogenation of cyclohexane and cyclohexene to give benzene as the selective product has been observed with Au/TiO_2, Pd/TiO_2 and $AuPd/TiO_2$ catalysts. For cyclohexane at low conversion the primary reaction pathway is oxidative dehydrogenation. However, at the higher temperatures required for conversions of cyclohexane above 80% oxidation of the desired product is also observed leading to lower selectivities. Titania supported palladium enhances the activity significantly permitting the use of lower temperatures leading to enhanced benzene selectivities. No synergistic enhancement in rate of reaction is observed on the addition of gold to palladium in these supported nanoparticles as we consider that the solubility of hydrogen in palladium plays a role in the initial dehydrogenation reaction. We consider that with further catalyst design and optimisation a supported palladium catalyst could provide a useful means of purifying benzene by oxidative dehydrogenation of hydrocarbon impurities.

Acknowledgement

We wish to thank the Leverhulme Trust and also we thank King Abdul Aziz University (Saudi Arabia Government) for financial support.

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