

## The effect of ring size on the selective oxidation of cycloalkenes using supported metal catalysts

Cite this: *Catal. Sci. Technol.*, 2013, **3**, 1531

Hamed Alshammari, Peter J. Miedziak, David W. Knight, David J. Willock and Graham J. Hutchings\*

In this work we expand on our previous studies on the oxidation of cyclic alkenes using supported gold nanoparticles together with catalytic amounts of peroxides. We demonstrate that various sized cyclic alkenes can be oxidised by this catalyst, under green conditions, without solvent and using air as the oxidant gas. The effect of support, preparation method and choice of metal have been investigated, we demonstrate that supported gold is superior to palladium or a gold palladium alloy, we show that oxides provide the best support for these gold catalysts and the preparation methods that afford the smallest particles are the most active. We show that the reactivity of the cyclic alkenes is related to the ring size with the smaller rings more reactive than the larger rings at the same temperature. The selectivity to the epoxide is dependent on the size of the cyclic alkene ring. In particular, the epoxide selectivity is very low for rings containing fewer than seven carbon atoms. We discuss the origins of this selectivity effect, using DFT calculations to investigate the effect of ring strain on the intermediates and reaction products.

Received 16th December 2012,  
Accepted 3rd March 2013

DOI: 10.1039/c3cy20864h

[www.rsc.org/catalysis](http://www.rsc.org/catalysis)

## Introduction

Oxidation is a key process for commercial applications, in the production of chemical intermediates, high tonnage commodity chemicals, high value fine chemicals, agrochemicals and pharmaceuticals. These oxidations often use stoichiometric oxygen donors such as chromate or permanganate, oxygen donors that give rise to pollutants of considerable environmental concern.<sup>1</sup> Accordingly, research to find green alternatives is now attracting considerable interest, as replacement production processes are crucial to providing cleaner routes to important oxidation products. The ultimate goal is to employ dioxygen with an efficient oxidation catalyst. Gold catalysts<sup>2</sup> have been shown to be effective for several types of oxidation reaction particularly the oxidation of alcohols,<sup>3–5</sup> oxidative esterification of alcohols,<sup>6,7</sup> the direct synthesis of hydrogen peroxide<sup>8</sup> and the oxidation of alkenes. The epoxidation of ethene using molecular oxygen is carried out industrially using a silver catalyst<sup>9,10</sup> but higher alkenes are generally epoxidised using hydrogen peroxide.<sup>11–16</sup>

In recent years there has been a considerable interest in the use of supported gold nanoparticles as catalysts for redox reactions.<sup>17–20</sup> The reactions include the oxidation of alcohols,

as well as the selective oxidation of CO in the presence of H<sub>2</sub>.<sup>21</sup> Epoxidation of cyclic alkenes has also been studied using supported gold catalysts.<sup>22–26</sup> It has previously been demonstrated that cyclohexene can be oxidised to the epoxide using a gold catalyst, a catalytic amount of *tert*-butyl hydroperoxide (TBHP) and molecular oxygen, with the selectivity to the epoxide strongly dependant on the choice of solvent, with non-polar solvents the most selective to C<sub>6</sub> products and polar solvents leading to the formation of formic acid and CO<sub>2</sub>.<sup>22</sup> In the same work it was demonstrated that cyclooctene can be oxidised under similar conditions but in the absence of solvent with high selectivity to the epoxide. Oxidation of cyclooctene can be carried out by using a range of radical initiators in catalytic amounts.<sup>23,24</sup> Tsang *et al.*<sup>27</sup> showed that by using gold nanoparticles supported on Si nanowires (SiNWs) as a catalyst, high conversion of cycloalkenes can be obtained. In their work cyclohexene was oxidized with 92% conversion and with 75% selectivity to 2-cyclohexen-1-ol in the presence of TBHP. However, selectivity to cyclohexene oxide was very low when the reaction was carried out under solvent free conditions. In contrast, cyclooctene oxidation proceeded with 38% conversion and 90% selectivity to cyclooctene oxide in the presence of TBHP under mild reaction conditions. The authors suggest that the high activity of catalyst is due to the high surface area of the SiNWs giving them the ability to support high metal loadings (up to 20 wt%).

Cardiff Catalysis Institute, School of Chemistry, Cardiff University,  
Cardiff CF10 3AT, UK. E-mail: hutch@cardiff.ac.uk

Li *et al.*<sup>28</sup> have reported the use of gold supported on carbon nanotubes as catalysts for the oxidation of cyclooctene to cyclooctene oxide. They found that 54% conversion and 44% selectivity to cyclooctene oxide could be obtained when using CH<sub>3</sub>CN as solvent in presence of TBHP.

Corma and co-workers<sup>25</sup> demonstrated that 2,2-azoisobutyronitrile (AIBN) can also be used as a radical initiator for cyclohexene oxidation at 60 °C using a Au/CeO<sub>2</sub> catalyst, so that oxygen from the radical initiator is not required in these reactions. In their work cyclohexene oxide was obtained with 20% selectivity and a selectivity of 15% of 2-cyclohexen-1-ol was achieved. The importance of the radical initiator was confirmed by showing that negligible conversion is observed in absence of AIBN.

Work on the oxidation of cyclooctene by Bawaked *et al.*<sup>23,24</sup> used a wide range of supports for gold catalysts. Therein it was demonstrated that the activity for cyclooctene oxidation of Au supported on different materials follows the order: graphite ≈ SiC > Al<sub>2</sub>O<sub>3</sub> ≈ SiO<sub>2</sub> > TiO<sub>2</sub> and the trend for selectivity to the epoxide was: graphite ≈ SiO<sub>2</sub> ≈ TiO<sub>2</sub> > SiC > Al<sub>2</sub>O<sub>3</sub>. Earlier work also evaluated the influence of preparation method on cyclooctene epoxidation, the sol-immobilisation method led to more active catalysts for epoxidation than alternative approaches.

We have demonstrated that alloying gold with palladium leads to an enhancement in activity and selectivity for a number of reactions. For example, we observed a twenty five-fold enhancement in activity for the oxidation of 1-phenylethanol when a 1:1 Au:Pd weight ratio catalysts was used.<sup>4</sup> These bi-metallic catalysts also markedly improve the yield of hydrogen peroxide in its direct synthesis from hydrogen and oxygen. In these earlier studies we used a wet impregnation preparation method to generate the gold–palladium nanoparticles.

In this contribution we expand on our previous study of cyclooctene epoxidation using supported gold nanoparticles and investigate the effect of ring size on the oxidation of cyclic alkenes using supported gold and gold–palladium nanoparticles under solvent free conditions using air as the oxidant with catalytic amounts of radical initiator. We investigate the effect of reaction temperature, the support and the preparation method on a range of cyclic alkenes. We find that the selectivity to epoxide changes significantly as a function of ring size.

We will also discuss the mechanism of the oxidation reactions based on DFT calculations. Corma and co-workers have used DFT calculations to suggest that reactive oxygen species can be formed on Au<sub>38</sub> clusters which can react with ethene to form ethylene oxide. However, when the calculations were carried out with propene they find that β-hydride abstraction occurs with a lower barrier than direct epoxidation.<sup>29</sup> The cycloalkenes also have β-hydrogen atoms available and so direct oxidation of the alkene double bond by a surface oxygen species is unlikely. Accordingly, we have concentrated on the β-hydride abstraction mechanism. We have calculated potential energy surfaces for cyclopentene and cyclooctene to compare the potential energy barriers for the formation of intermediates

that result in epoxide formation to understand the different reaction pathways for different size cyclic alkenes. This information gives an insight into the origin of the observed selectivity differences for cyclic alkenes with different ring sizes.

## Experimental

### Catalyst preparation

For all catalysts the metal concentrations are expressed as percentage metal by weight, *i.e.* weight of metal relative to total weight of metal and support. Catalysts were prepared using the following standard methods.

### Sol-immobilisation

1%Au, Pd and Au–Pd bimetallic catalysts were prepared by the sol-immobilisation method. For example a 0.5%Au + 0.5%Pd/graphite (G) catalyst was prepared as follows: solutions of PdCl<sub>2</sub>(aq) (Johnson Matthey, 6 mg in 1 ml) and HAuCl<sub>4</sub>·3H<sub>2</sub>O(aq) (Johnson Matthey, 12.25 g in 1000 ml) were prepared. Polyvinyl alcohol(aq) (PVA) (1 wt% solution, Aldrich,  $M_w = 10\,000$ , 80% hydrolyzed) was added to the solution and stirred with HAuCl<sub>4</sub>·3H<sub>2</sub>O for 15 min. 0.1 M of NaBH<sub>4</sub>(aq) (>96% Aldrich, NaBH<sub>4</sub>/Au (mol/mol = 5)) was freshly prepared and then added to form a dark brown sol. The mixture was stirred for 30 min and adjusted to pH 1 by the drop-wise addition of sulphuric acid. Graphite (Aldrich) (1.98 g) was then added to the mixture. Following which the slurry was stirred for 1 h after which the catalyst was recovered by filtration, washed with 2 L distilled water and dried at 110 °C overnight. The characterisation of these catalyst has been reported previously,<sup>30</sup> the metal particle size distribution was found to be in the range of 4–7 nm.

### Impregnation

A 1%Au/G catalyst was prepared as follows: A solution of HAuCl<sub>4</sub>·3H<sub>2</sub>O(aq) (12.25 g in 1000 ml) was added to graphite (0.99 g). The mixture was stirred for 5 min until a paste was formed, dried at 110 °C for 16 h then calcined at 400 °C for 3 h in static air. The characterisation of these catalysts has been reported previously,<sup>30</sup> showing that the particle size is distribution is largely contained between 2 and 14 nm with an average size around 6 nm. Although, occasional larger particles (>25 nm) were also reported.

### Deposition precipitation

A 1%Au/G catalyst was prepared by a deposition precipitation method. Graphite (0.99 g) was mixed with distilled water (150 ml) and stirred at 60 °C. A solution of HAuCl<sub>4</sub>·3H<sub>2</sub>O(aq) (12.25 g in 1000 ml) was added, and subsequently a solution of NaOH(aq) (1 M) was added drop-wise to the mixture to maintain an overall pH of 9. After 1.5 h the solution was filtered and washed with distilled water (1 L). The catalyst was dried at 110 °C for 16 h and calcined in static air at 400 °C for 3 h. Previously reported characterisation of catalysts prepared by this method<sup>31</sup> found that the metal particles were in the 2–10 nm range and XEDS revealed they were Au–Pd alloys in nature.

## Incipient wetness impregnation

A 1%Au/G catalyst was prepared using impregnation *via* an incipient wetness method. An aqueous solution of HAuCl<sub>4</sub>·3H<sub>2</sub>O(aq) (12.25 g dissolved in 1000 ml) was added to the support. The paste formed was dried at 110 °C for 16 h then calcined at 400 °C for 3 h in static air. This preparation method was reported by Baatz and Prüsse who found a bimodal particle size distribution, the sub-10 nm particles having an average size of 3.1 nm.<sup>32</sup>

## Catalyst testing

Oxidation of cycloalkenes (cyclopentene, cyclohexene, cycloheptene, cyclooctene and cyclododecene) using air were carried out in a glass reactor consisting of a 50 ml round-bottomed flask fitted with a reflux condenser. Typically, the catalyst (0.12 g) was suspended in the substrate (10 ml) without any solvent but with a small amount of radical initiator TBHP (0.1 ml, 70% in H<sub>2</sub>O). The reaction mixture was stirred for 24 h. A range of reaction temperatures were tested for each cyclic alkene with the upper limit in each case set by the boiling point: cyclopentene 22–30 °C, cyclohexene 40–60 °C, cycloheptene 50–70 °C, cyclooctene 70–90 °C and cyclododecene 120 °C. A sample of the reaction was taken for analysis after the reaction was completed. Analysis was carried out using gas chromatography (Varian star CP-3800) with a CP-wax 32 column and a flame ionization detector.

## Calculations

DFT calculations (B3LYP/6-311G+(d,p)) were carried out using the Gaussian03 suite of software.<sup>33</sup> Transition states were located using optimised scans with the high point on the resulting minimum energy pathway used in a transition state optimisation calculation. Minima and transition states were confirmed using frequency calculations, with all real (positive frequencies) modes indicating a minimum and all real except for a single imaginary (negative frequency) mode showing that a transition state had been located.

## Results and discussion

To test for auto-oxidation blank reactions using our standard reaction conditions and reagents but without the inclusion of catalyst were carried out for a range of temperatures, depending on the boiling point of the cyclic alkenes. It has previously been shown that the oxidation of cyclic alkenes requires a radical initiator and for this reason we have used a catalytic amount of TBHP in this study.<sup>22–26</sup> In the range of temperatures selected the conversion of the alkenes was generally very low (<1%) (Table 1), the exceptions to this were cycloheptene, which had a maximum conversion of 6.5% at 70 °C, and cyclododecene, of which 4.8% was converted at 120 °C. The effect of the addition of the graphite support to these reactions is also shown in Table 1. In most cases the presence of graphite does not make a significant difference to the conversion of the cyclic alkene. In the case of cyclooctene at 90 °C there is a

**Table 1** Comparison of oxidation activity for cycloalkenes with TBHP, in the presence of support material and in the presence of 1%Au/G catalyst

	Temperature	Conversion (%)	Selectivity		
			Epoxide	Cy-one	Cy-ol
Cyclopentene <sup>a</sup>	22 Blank	0.08	4	49	46
	26 Blank	0.1	7.3	65.6	27
	30 Blank	0.1	3.8	33.2	34.4
	22 Graphite	0.1	3.2	36.4	39
	26 Graphite	0.2	5.3	42.9	41.6
	30 Graphite	0.4	7.9	39.7	37.6
	22 1%Au/G	2.2	17.2	43	23
	26 1%Au/G	4.4	12.4	43.6	23.9
	30 1%Au/G	8.3	10.9	43.3	33.3
Cyclohexene <sup>b</sup>	40 Blank	0.01	0	43.9	56.1
	50 Blank	0.04	4.6	52.8	42.6
	60 Blank	0.05	4.3	51.5	44.3
	40 Graphite	0.01	0	48	52
	50 Graphite	0.03	0	49.3	41.9
	60 Graphite	0.14	4.3	49.5	43.8
	40 1%Au/G	6.5	8.2	43.3	45.5
	50 1%Au/G	8.2	6.4	50.5	41.4
	60 1%Au/G	11.6	5.9	53.8	40.2
Cycloheptene <sup>c</sup>	50 Blank	1.7	15.3	26.5	58.2
	60 Blank	2	24	31	44
	70 Blank	6.5	24	26	48
	50 Graphite	2.4	13	26.5	60.5
	60 Graphite	4.9	17.6	29.5	52.9
	70 Graphite	6.2	34.4	34.9	30.6
	50 1%Au/G	9	17.8	35.2	47
	60 1%Au/G	10.1	18.2	43.5	38.4
	70 1%Au/G	11.2	19.8	47.9	32.3
Cyclooctene <sup>d</sup>	70 Blank	0.01	56.1	0	43.9
	80 Blank	0.03	47.6	13.1	39.3
	90 Blank	0.2	65.1	1.1	8.8
	70 Graphite	0.1	66.8	5.3	27.8
	80 Graphite	0.4	79.7	4.5	15.8
	90 Graphite	5.4	86.3	4.7	7.2
	70 1%Au/G	2.6	81.1	6.3	12.6
	80 1%Au/G	6.8	85.9	4.8	9.3
	90 1%Au/G	11.5	86.3	5.3	7.8
Cyclododecene <sup>e</sup>	120 Blank	4.8	75	23	—
	120 Graphite	8	88	10	—
	120 1%Au/G	10.2	60.5	37	—

Reaction conditions: 10 ml of substrate, TBHP ( $0.064 \times 10^{-3}$  mol), glass reactor, 24 h, atmospheric pressure. <sup>a</sup> Substrate : metal (mol : mol) = 18 017, substrate : TBHP (mol : mol) = 1707. <sup>b</sup> Substrate : metal (mol : mol) = 16 289, substrate : TBHP (mol : mol) = 1543. <sup>c</sup> Substrate : metal (mol : mol) = 14 135, substrate : TBHP (mol : mol) = 1339. <sup>d</sup> Substrate : metal (mol : mol) = 12 664, substrate : TBHP (mol : mol) = 1220. <sup>e</sup> Substrate : metal (mol : mol) = 8560, substrate : TBHP (mol : mol) = 811.

significant increase in the conversion upon the addition of graphite to the reaction mixture, from 0.2 to 5.4%. An increase in conversion is also observed for cyclododecene oxidation, which is also carried out at an elevated temperature, 120 °C, suggesting that at higher temperatures graphite alone can catalyse the reaction. We have previously observed that graphite can act as a catalyst for the oxidation of cyclooctene at temperatures of  $\geq 100$  °C.<sup>23</sup> The addition of gold supported on graphite, however, leads to a significant increase in the conversion of the cyclic alkenes at all the reaction temperatures studied.

Table 1 shows that oxidation of the larger ring sizes requires the use of higher temperatures. This makes direct comparison of the reactivity of the alkenes difficult. However, referring to Table 1 we note that, at 30 °C, cyclopentene gives comparable conversion over 1%Au/G to cyclohexene at 50 °C, suggesting the smaller ring is more reactive toward oxidation. The conversion of cyclohexene at 50 °C and cycloheptene at 60 °C appear similar for the supported Au catalyst but the significantly higher reactivity in the absence of Au for cycloheptene may suggest that the metal catalysed conversion of cyclohexene is actually the greater. As we move to cyclooctene and cyclododecene higher temperatures are required and yet conversions using 1%Au/G do not significantly increase. These observations suggest that the reactivity of the cyclic alkenes decreases as the ring size increases.

Alloying gold with a second metal has been shown to lead to a considerable increase in the activity of gold catalysts, particularly for the oxidation of alcohols<sup>4,34–36</sup> and the selective oxidation of toluene.<sup>37,38</sup> To see if a similar effect could be observed for the oxidation of cyclic alkenes a series of bimetallic gold palladium catalysts were synthesised using the sol-immobilisation method. The conversions and selectivities for these catalysts are shown in Table 2. It is clear that the effects previously reported for bimetallic catalytic oxidation reactions are not observed with the oxidation of cyclic alkenes. The bimetallic catalyst is not the most active catalyst for any of the cycloalkenes studied, in fact with each substrate the gold monometallic catalyst gives the highest conversion. In most cases the palladium catalyst shows the lowest activity, however some activity is observed compared to the blank reactions. The bimetallic catalysts tend to have an activity between that observed for the monometallic catalysts suggesting that palladium is, in this case, acting as an inhibitor or a diluent for

the active gold phase. There does appear to be a significant trend between the metal and the selectivity towards the major products, although it appears that the previously discussed trend towards the epoxide with the larger ring size still applies whichever metal is present in the catalyst, however it is observed that for the smaller ring sizes the addition of palladium to the catalyst leads to an increase in the selectivity of the diol product.

Previous studies on gold catalysts have shown a significant support effect on both the conversion and selectivity. A series of gold catalysts were prepared on a range of oxide supports and these were tested for the oxidation for the different cyclic alkenes, the results are shown in Table 3. Initially the bare supports were tested, for the majority of the alkenes there was no significant improvement in conversion compared to the blank tests (Table 1), the notable exceptions were cycloheptene and cyclododecene. In the case of cycloheptene it is only the graphite support that leads to a significantly enhanced conversion. In the case of cyclododecene there is significant conversion with any of the supports tested, however, this may be associated with the temperature that these reactions were carried out at, as discussed previously. The addition of gold to the support in all cases leads to a significant enhancement in the conversion of the substrate. The enhancement in the conversion is most significant at lower temperatures with cyclopentene and cyclohexene displaying the greatest improvement when compared to both the blank reaction and reaction of the bare support. For all the supports tested, the same selectivity trend as has been previously discussed with the gold on graphite catalyst is found. The selectivity towards the epoxide product is considerably greater for cyclooctene and cyclododecene than it is for the smaller ring cycloalkenes. All of the supports tested for this reaction showed similar activities,

**Table 2** Effect of alloying metal on cycloalkene epoxidation

	Temperature (°C)	Catalyst	S : M ratio (mol : mol)	Conversion (%)	Selectivity (%)		
					Epoxide	Cy-one	Cy-ol
Cyclopentene <sup>a</sup>	26	Au/G	18 017	4.4	12.4	43.6	23.9
		Au-Pd/G	12 599	3.5	14.7	20.9	36.9
		Pd/G	9686	1.4	11.8	20.1	38.4
Cyclohexene <sup>b</sup>	50	Au/G	16 288	8.2	6.4	50.5	41.4
		Au-Pd/G	11 389	4.5	6.6	14.4	78.9
		Pd/G	8756	2.5	15.2	32.2	50.8
Cycloheptene <sup>c</sup>	60	Au/G	14 135	10.1	18.2	43.5	38.4
		Au-Pd/G	9884	7.8	16.7	40.6	42.7
		Pd/G	7599	9.6	20.2	30.4	49.5
Cyclooctene <sup>d</sup>	80	Au/G	12 664	6.8	85.9	4.8	9.3
		Au-Pd/G	8856	2.5	85	5.4	9.6
		Pd/G	6808	2.8	85.4	5.3	9.4
Cyclododecene <sup>e</sup>	120	Au/G	8561	10.2	60.5	37	—
		Au-Pd/G	5986	8.2	81.2	16	—
		Pd/G	4602	10	65.7	10.3	—

Reaction conditions: 10 ml of substrate, 0.12 g of catalyst, TBHP ( $0.064 \times 10^{-3}$  mol), glass reactor, 24 h, atmospheric pressure. <sup>a</sup> Substrate : TBHP (mol : mol) = 1707. <sup>b</sup> Substrate : TBHP (mol : mol) = 1543. <sup>c</sup> Substrate : TBHP (mol : mol) = 1339. <sup>d</sup> Substrate : TBHP (mol : mol) = 1220. <sup>e</sup> Substrate : TBHP (mol : mol) = 811.

**Table 3** Effect of support on cycloalkene epoxidation using 1%Au/support

	Temperature (°C)	Catalyst	Conversion (%)	Selectivity		
				Epoxide	Cy-one	Cy-ol
Cyclopentene <sup>a</sup>	26	Graphite	0.2	5.3	42.9	41.6
		1%Au/Graphite	4.4	12.4	43.6	23.9
		TiO <sub>2</sub>	1.3	12	44	26
		1%Au/TiO <sub>2</sub>	5.7	11.3	40.2	25.2
		SiO <sub>2</sub>	0.2	20	25	49
		1%Au/SiO <sub>2</sub>	5.2	9	44.8	11.5
		CeO <sub>2</sub>	0.2	10	32	47
		1%Au/CeO <sub>2</sub>	7	12.8	37.2	21.9
Cyclohexene <sup>b</sup>	50	Graphite	Trace	0	69.8	30.2
		1%Au/Graphite	4.4	12.4	43.6	23.9
		TiO <sub>2</sub>	Trace	0	68.0	31.0
		1%Au/TiO <sub>2</sub>	6.7	9.9	25.6	61.2
		SiO <sub>2</sub>	0	0	0	0
		1%Au/SiO <sub>2</sub>	7.9	6.2	51.1	41.8
		CeO <sub>2</sub>	0.4	3.4	89	4.3
		1%Au/CeO <sub>2</sub>	6.2	7.8	42.0	49.0
Cycloheptene <sup>c</sup>	60	Graphite	4.9	17.6	29.5	52.9
		1%Au/Graphite	10.1	18.2	43.5	38.4
		TiO <sub>2</sub>	3.0	21.0	25.0	53.0
		1%Au/TiO <sub>2</sub>	10.7	19.1	42.7	38.2
		SiO <sub>2</sub>	2.5	21	44	34
		1%Au/SiO <sub>2</sub>	14.1	18	40.5	41.5
		CeO <sub>2</sub>	2	23	40	36
		1%Au/CeO <sub>2</sub>	9.6	20.7	35.9	43.4
Cyclooctene <sup>d</sup>	80	Graphite	0.4	17.6	29.5	52.9
		1%Au/Graphite	6.8	85.9	4.8	9.3
		TiO <sub>2</sub>	0.2	33	33	36
		1%Au/TiO <sub>2</sub>	6.6	81.4	5	7.6
		SiO <sub>2</sub>	0.1	50	20	30
		1%Au/SiO <sub>2</sub>	4.6	87.4	5	7.7
		CeO <sub>2</sub>	1.9	81	4.8	10
		1%Au/CeO <sub>2</sub>	4.6	74.1	1.3	8.1
Cyclododecene <sup>e</sup>	120	Graphite	8	88	10	—
		1%Au/Graphite	10.2	60.5	37	—
		TiO <sub>2</sub>	7.3	91	8.2	—
		1%Au/TiO <sub>2</sub>	9.4	65.9	33	—
		SiO <sub>2</sub>	7.4	93	6.9	—
		1%Au/SiO <sub>2</sub>	8.6	60.9	35	—
		CeO <sub>2</sub>	8.8	89	10	—
		1%Au/CeO <sub>2</sub>	11.8	76.7	23	—

Reaction conditions: 10 ml of substrate, 0.12 g of catalyst, TBHP ( $0.064 \times 10^{-3}$  mol), glass reactor, 24 h, atmospheric pressure. <sup>a</sup> When gold is present, substrate : metal (mol : mol) = 18 017, substrate : TBHP (mol : mol) = 1707. <sup>b</sup> When gold is present, substrate : metal (mol : mol) = 16 289, substrate : TBHP (mol : mol) = 1543. <sup>c</sup> When gold is present, substrate : metal (mol : mol) = 14 135, substrate : TBHP (mol : mol) = 1339. <sup>d</sup> When gold is present, substrate : metal (mol : mol) = 12 664, substrate : TBHP (mol : mol) = 1220. <sup>e</sup> When gold is present, substrate : metal (mol : mol) = 8560, substrate : TBHP (mol : mol) = 811.

with SiO<sub>2</sub> generally being the either the most active support or showing very similar activity to the most active support in each case. The observation that different supports proved to be more active for different substrates in itself is not entirely unexpected as the interaction between the support and the substrate must play a role in the transport of the required chemicals to the active site of the catalyst.

To test the effect of the preparation method a series of 1%Au catalysts were prepared by a range of methods namely, impregnation, deposition precipitation and incipient wetness. These catalysts are compared to the sol-immobilisation prepared catalysts in Table 4. Although there was variation between the substrates in all cases the catalysts prepared using the

sol-immobilisation technique provided the most active catalyst. Previous work has shown that the sol-immobilisation method leads to catalysts with the narrowest particle size distribution of all the preparation methods used in this work.<sup>31,32,39</sup> There is also a notable difference between the catalysts prepared using the sol-immobilisation and deposition precipitation methods, which include a washing step and those that do not include washing, namely impregnation and incipient wetness. The higher activity of the washed catalysts suggests that the removal of excess chloride ions has a beneficial influence on the activity. It has been previously reported that excess surface chloride ions can form bridging bonds with gold particles leading to particle growth, the higher activity is displayed when this washing step

**Table 4** Effect of the preparation methods on cycloalkene epoxidation using 1%Au/G

	Temperature (°C)	Method	Conversion (%)	Selectivity		
				Epoxide	Cy-one	Cy-ol
Cyclopentene <sup>a</sup>	26	Sol-immobilisation	4.4	12.4	43.6	23.9
		Impregnation	1.3	16	28	36
		Deposition precipitation	1.8	10.7	49.4	39.9
		Incipient wetness	1.1	12.3	34.7	36.7
Cyclohexene <sup>b</sup>	50	Sol-immobilisation	8.2	6.4	50.5	41.4
		Impregnation	6.02	6.6	16.3	77
		Deposition precipitation	4.5	11.5	42	45
		Incipient wetness	2.75	5.5	22.4	69
Cycloheptene <sup>c</sup>	60	Sol-immobilisation	10.1	18.2	43.5	38.4
		Impregnation	6.6	17.3	33.2	49.5
		Deposition precipitation	7.6	18.1	30.7	51.2
		Incipient wetness	6.5	19.8	28.8	51.4
Cyclooctene <sup>d</sup>	80	Sol-immobilisation	6.8	85.9	4.8	9.3
		Impregnation	3.2	86.3	4.5	9.2
		Deposition precipitation	3.7	80.2	4.1	15.7
		Incipient wetness	4.3	88.7	1.6	9.7
Cyclododecene <sup>e</sup>	120	Sol-immobilization	10.2	60.5	37	—
		Impregnation	9.2	66.4	33	—
		Deposition precipitation	9.0	65	34	—
		Incipient wetness	9.7	66.5	33	—

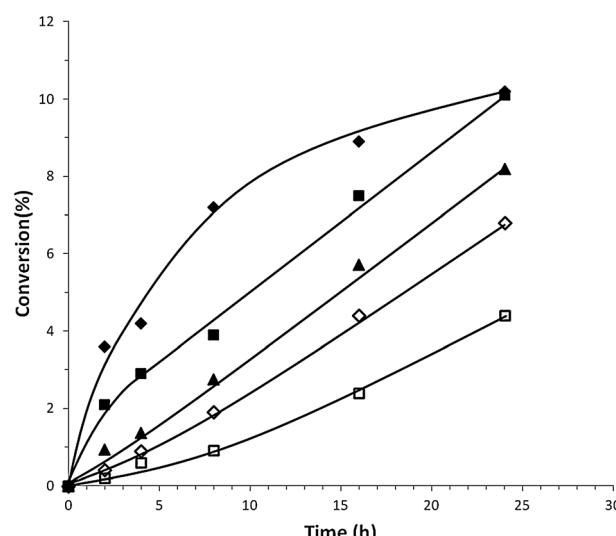
Reaction conditions: 10 ml of substrate, 0.12 g of catalyst, TBHP ( $0.064 \times 10^{-3}$  mol), glass reactor, 24 h, atmospheric pressure. <sup>a</sup> Substrate : metal (mol : mol) = 18 017, substrate : TBHP (mol : mol) = 1707. <sup>b</sup> Substrate : metal (mol : mol) = 16 289, substrate : TBHP (mol : mol) = 1543. <sup>c</sup> Substrate : metal (mol : mol) = 14 135, substrate : TBHP (mol : mol) = 1339. <sup>d</sup> Substrate : metal (mol : mol) = 12 664, substrate : TBHP (mol : mol) = 1220.

<sup>e</sup> Substrate : metal (mol : mol) = 8560, substrate : TBHP (mol : mol) = 811.

is carried out supporting the theory that for these reactions small gold particles are vital. At the higher temperatures used for the oxidation of cyclododecene all catalysts performed similarly, once again suggesting that at this temperature auto-oxidation is the principal mechanism.

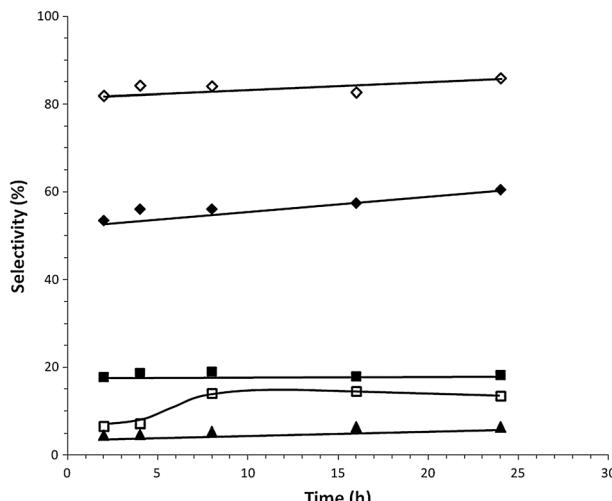
Finally, using the optimised conditions, time on line studies were carried out for each of the cyclic alkenes, the results are shown in Fig. 1 and 2. Fig. 1 shows the conversion of the cycloalkenes as a function of time. Generally the trend shown is that conversion increases as the size of the ring increases. However, it must be kept in mind that the temperature of the reaction is also higher for the larger cycloalkenes. Fig. 2 shows the selectivity towards the epoxide, there is a clear bimodal distribution in the selectivities, with the previously discussed trend outlined by the time on line data. At the conversion levels achieved in this work the selectivity towards the epoxide product is constant over the time period studied for all substrates.

There is a significant trend in the selectivity to the epoxide when the gold catalyst is present. The selectivity is relatively low for the smaller ring sizes (between 6 and 20% for C<sub>5</sub>–C<sub>7</sub>), increasing significantly for the C<sub>8</sub> and C<sub>12</sub> rings. In our previous discussion of the mechanism of oxidation in this system<sup>24</sup> we have proposed a catalytic cycle involving radical species. The mechanism is shown in Scheme 1 using cyclopentane as an example substrate. The scheme is drawn to emphasise how the oxidation products observed can be explained. The reaction is initiated by cleavage of the <sup>t</sup>BuO-OH bond over the surface of an Au particle to form surface bound radicals. This reaction has

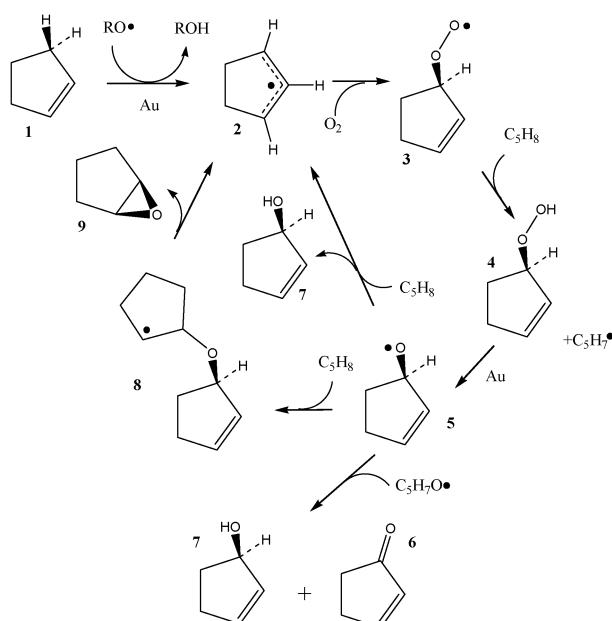


**Fig. 1** Effect of reaction time for the conversion of cycloalkene. Reaction conditions: 10 ml of substrate, 0.12 g of catalyst, TBHP ( $0.064 \times 10^{-3}$  mol), glass reactor, atmospheric pressure. □ cyclopentene<sup>a</sup> (26 °C), ▲ cyclohexene<sup>b</sup> (50 °C), ■ cycloheptene<sup>c</sup> (60 °C), △ cyclooctene<sup>d</sup> (80 °C) and ◆ cyclododecene<sup>e</sup> (120 °C). Substrate : metal (mol : mol) = <sup>a</sup>18 017, <sup>b</sup>16 289, <sup>c</sup>14 135, <sup>d</sup>12 664, <sup>e</sup>8560. Substrate : TBHP (mol : mol) = <sup>a</sup>1707, <sup>b</sup>1543, <sup>c</sup>1339, <sup>d</sup>1220, <sup>e</sup>811.

been found to be energetically favourable and practically barrierless in DFT calculations.<sup>40</sup> These surface radicals can abstract hydrogen from one of the allylic positions to give the radical, 2. In turn 2 will capture molecular oxygen to form a



**Fig. 2** Effect of reaction time for the selectivity of epoxidation of cycloalkene. Reaction conditions: 10 ml of substrate, 0.12 g of catalyst, TBHP ( $0.064 \times 10^{-3}$  mol), cyclopentene<sup>a</sup> (26 °C), cyclohexene<sup>b</sup> (50 °C), cycloheptene<sup>c</sup> (60 °C), cyclooctene<sup>d</sup> (80 °C) and cyclododecene<sup>e</sup> (120 °C), glass reactor, atmospheric pressure. □ cyclopentene oxide and ◆ cyclohexene oxide, ■ cycloheptene oxide, ◇ cyclooctene oxide and ▲ cyclododecene oxide. Substrate: metal (mol : mol) = <sup>a</sup>18017, <sup>b</sup>16289, <sup>c</sup>14135, <sup>d</sup>12664, <sup>e</sup>8560. Substrate: TBHP (mol : mol) = <sup>a</sup>1707, <sup>b</sup>1543, <sup>c</sup>1339, <sup>d</sup>1220, <sup>e</sup>811.



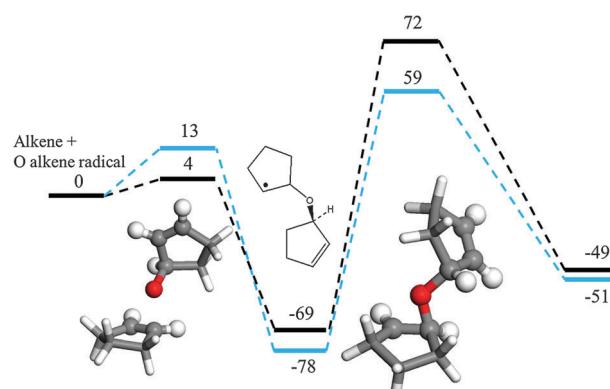
**Scheme 1** A proposed mechanism for the oxidation of cyclopentene which would lead to the observed products.

peroxy radical, 3, which can then abstract hydrogen from another molecule of substrate to produce the hydroperoxide, 4, and further carbon centred radical, 2. Again, invoking the RO-OH cleavage reaction over the surface of Au particles the radical, 5, is generated. At this point there are three possibilities; firstly 5 can react with further substrate with H abstraction from an allylic position to produce an alcohol, 7, and a further allylic

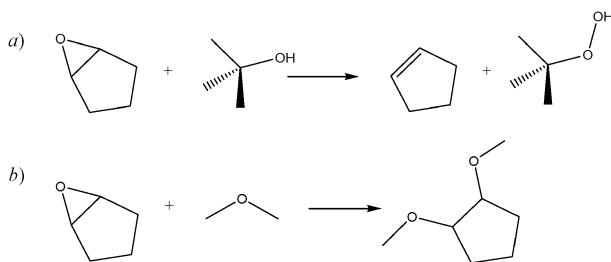
radical. Secondly, interaction between 5 and the double bond of the cycloalkene will result in the intermediate, 8, which can ring close to form the epoxide product, 9, and a further allylic radical. Either of these pathways generates the allylic radical, 2, and so the reaction can continue to consume more substrate. The third alternative involves the reaction of two molecules of 5 via H abstraction to produce the allylic ketone, 6 and the alcohol, 7. In this case radical species are lost and so this can be thought of as the termination step of the process.

In the mechanism set out in Scheme 1 the selectivity of the reaction is controlled by the relative importance of the three reaction pathways available to the allylic oxygen radical, 5. We have carried out a series of DFT calculations to consider the effect of ring size on the production and reaction of 5 by comparing the potential energy surfaces calculated for cyclopentene and cyclooctene. Fig. 3 shows that for both the cyclopentene and the cyclooctene systems the formation of intermediate 8 is both energetically favourable and occurs with a small potential energy barrier. However, for the C<sub>5</sub> ring system the barrier to ring closure to form the epoxide is 13 kJ mol<sup>-1</sup> higher than that for the C<sub>8</sub> case. Hence, for the C<sub>8</sub> system, once the intermediate is formed, it is more likely that an epoxide will be produced than in the C<sub>5</sub> ring case.

One possible origin of the difference in energy for the C<sub>5</sub> and C<sub>8</sub> ring closure transition states is additional ring strain that may be expected when an epoxide is formed on a small (e.g. C<sub>5</sub>) alkene ring compared to that for the more flexible larger rings of C<sub>8</sub> and greater. To test this computationally we consider two reactions in which the epoxide ring is opened;<sup>41</sup> Scheme 2a gives the reverse epoxidation reaction with TBHP and Scheme 2b shows a simple etherolysis with dimethylether (DME). The etherolysis reaction is particularly interesting because it is an isodesmic reaction; i.e. there is the same number of each type of chemical bond present in reactants and products so that effects due to changes in bond types are minimised. Table 5 shows that in both cases the reaction energy calculated for the C<sub>5</sub> and C<sub>8</sub> systems are within 10 kJ mol<sup>-1</sup> of one another based on the electronic energies alone and come into even closer



**Fig. 3** Calculated potential energy surface for the formation of intermediate 5 and ring closure to form the epoxide product, 9 for C<sub>5</sub>(black) and C<sub>8</sub>(blue) systems. Calculated at the B3LYP/6-31G(d,p) level. For the molecular graphic insets atoms colours follow; C = grey, O = red and H = white.



**Scheme 2** Reactions used to estimate epoxide ring strain based on B3LYP/6-31G(d,p) level calculations. (a) The reverse epoxidation reaction and (b) etherolysis.

**Table 5** The calculated reaction energy of the C<sub>5</sub> and C<sub>8</sub> systems for reverse epoxidation and etherolysis

Reaction	C <sub>5</sub> /kJ mol <sup>-1</sup>	C <sub>8</sub> /kJ mol <sup>-1</sup>	C <sub>5</sub> -C <sub>8</sub> /kJ mol <sup>-1</sup>
Reverse epoxidation	195 (185)	188 (181)	7 (4)
Etherolysis	-76 (-20)	-83 (-25)	13 (5)

agreement when free energy corrections are included. This suggests that if the difference in transition state energies is due to differences in ring strain energy of C<sub>8</sub> and C<sub>5</sub> epoxides it is not carried over into the products.

## Conclusions

We have carried out a thorough investigation into the oxidation of various cyclic alkenes ranging in ring size from 5 to 12 carbons. We have shown the gold is a better catalyst for these substrates than either palladium or a gold–palladium alloy. The greatest activity for the gold catalysts was shown when the catalyst preparation method used gave smaller metal particles and also incorporate a washing step into the preparation, *i.e.* the sol immobilisation and deposition precipitation methods. When the oxidations are considered at iso-temperature it is clear that the smaller rings are more reactive than the larger rings, however, the higher boiling points of the larger rings facilitates reaction at higher temperatures and therefore higher conversion. With the larger rings (C<sub>8</sub>–C<sub>12</sub>) the selectivity towards the epoxide is significantly higher than the smaller rings (C<sub>5</sub>–C<sub>7</sub>), DFT calculations indicate that the barrier to ring closure of radical intermediate is much greater for the smaller ring sizes.

## Acknowledgements

We would like to thank Hail University (Saudi Arabia) for financial support. Calculations were carried out using the Cardiff University ARCCA facility.

## References

- R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, 1981.
- A. S. K. Hashmi and G. J. Hutchings, *Angew. Chem., Int. Ed.*, 2006, **45**, 7896–7936.
- S. Biella, L. Prati and M. Rossi, *Inorg. Chim. Acta*, 2003, **349**, 253–257.
- D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Science*, 2006, **311**, 362–365.
- D. I. Enache, D. W. Knight and G. J. Hutchings, *Catal. Lett.*, 2005, **103**, 43.
- E. Taarning, A. T. Madsen, J. M. Marchetti, K. Egeblad and C. H. Christensen, *Green Chem.*, 2008, **10**, 408–414.
- G. L. Brett, P. J. Miedziak, N. Dimitratos, J. A. Lopez-Sanchez, N. F. Dummer, R. Tiruvalam, C. J. Kiely, D. W. Knight, S. H. Taylor, D. J. Morgan, A. F. Carley and G. J. Hutchings, *Catal. Sci. Technol.*, 2012, **2**, 97–104.
- P. Landon, P. J. Collier, A. J. Papworth, C. J. Kiely and G. J. Hutchings, *Chem. Commun.*, 2002, 2058–2059.
- K. Weissermel and H.-J. Arpe, *Industrial Organic Chemistry*, 4th edn, Weinheim, Wiley VCH, 2003.
- R. M. Lambert, F. J. Williams, R. L. Cropley and A. Palermo, *J. Mol. Catal. A: Chem.*, 2005, **228**, 27–33.
- D. Yin, L. Qin, J. Liu, C. Li and Y. Jin, *J. Mol. Catal. A: Chem.*, 2005, **240**, 40–48.
- N. S. Patil, B. S. Uphade, P. Jana, R. S. Sonawane, S. K. Bhargava and V. R. Choudhary, *Catal. Lett.*, 2004, **94**, 89–93.
- N. S. Patil, B. S. Uphade, P. Jana, S. K. Bhargava and V. R. Choudhary, *Chem. Lett.*, 2004, **33**, 400–401.
- P. Lignier, S. Mangematin, F. Morfin, J.-L. Rousset and V. Caps, *Catal. Today*, 2008, **138**, 50–54.
- C. Aprile, A. Corma, M. E. Domine, H. Garcia and C. Mitchell, *J. Catal.*, 2009, **264**, 44–53.
- P. Lignier, F. Morfin, L. Piccolo, J.-L. Rousset and V. Caps, *Catal. Today*, 2007, **122**, 284–291.
- G. C. Bond and D. T. Thompson, *Catal. Rev. Sci. Eng.*, 1999, **41**, 319–388.
- Q. Fu, H. Saltsburg and M. Flytzani-Stephanopoulos, *Science*, 2003, **301**, 935–938.
- J. E. Bailie and G. J. Hutchings, *Chem. Commun.*, 1999, 2151–2152.
- C. Mohr, H. Hofmeister, M. Lucas and P. Claus, *Chem. Eng. Technol.*, 2000, **23**, 324–328.
- H. Sakurai, A. Ueda, T. Kobayashi and M. Haruta, *Chem. Commun.*, 1997, 271–272.
- M. D. Hughes, Y.-J. Xu, P. Jenkins, P. McMorn, P. Landon, D. I. Enache, A. F. Carley, G. A. Attard, G. J. Hutchings, F. King, E. H. Stitt, P. Johnston, K. Griffin and C. J. Kiely, *Nature*, 2005, **437**, 1132–1135.
- S. Bawaked, N. F. Dummer, N. Dimitratos, D. Bethell, Q. He, C. J. Kiely and G. J. Hutchings, *Green Chem.*, 2009, **11**, 1037–1044.
- S. Bawaked, N. F. Dummer, D. Bethell, D. W. Knight and G. J. Hutchings, *Green Chem.*, 2011, **13**, 127–134.
- M. Álvaro, C. Aprile, A. Corma, B. Ferrer and H. García, *J. Catal.*, 2007, **245**, 249–252.
- S. Bawaked, Q. He, N. F. Dummer, A. F. Carley, D. W. Knight, D. Bethell, C. J. Kiely and G. J. Hutchings, *Catal. Sci. Technol.*, 2011, **1**, 747–759.

- 27 C. H. A. Tsang, Y. Liu, Z. Kang, D. D. D. Ma, N.-B. Wong and S.-T. Lee, *Chem. Commun.*, 2009, 5829–5831.
- 28 B. Li, P. He, G. Yi, H. Lin and Y. Yuan, *Catal. Lett.*, 2009, **133**, 33–40.
- 29 M. Boronat and A. Corma, *J. Catal.*, 2011, **284**, 138–147.
- 30 J. A. D. Lopez-Sanchez, N. Dimitratos, P. Miedziak, E. Ntanjua, J. K. Edwards, D. Morgan, A. F. Carley, R. Tiruvalam, C. J. Kiely and G. J. Hutchings, *Phys. Chem. Chem. Phys.*, 2008, **10**, 1921.
- 31 P. J. Miedziak, Q. He, J. K. Edwards, S. H. Taylor, D. W. Knight, B. Tarbit, C. J. Kiely and G. J. Hutchings, *Catal. Today*, 2011, **163**, 47–54.
- 32 C. Baatz and U. Prüße, *J. Catal.*, 2007, **249**, 34–40.
- 33 R. C. M. J. Frisch, *et al.*, *Gaussian 03*, Gaussian, Inc., Wallingford, CT, 2004.
- 34 A. Abad, C. Almela, A. Corma and H. Garcia, *Chem. Commun.*, 2006, 3178–3180.
- 35 A. Villa, N. Janjic, P. Spontoni, D. Wang, D. S. Su and L. Prati, *Appl. Catal., A*, 2009, **364**, 221–228.
- 36 J. Pritchard, L. Kesavan, M. Piccinini, Q. He, R. Tiruvalam, N. Dimitratos, J. A. Lopez-Sanchez, A. F. Carley, J. K. Edwards, C. J. Kiely and G. J. Hutchings, *Langmuir*, 2010, **26**, 16568–16577.
- 37 M. I. bin Saiman, G. L. Brett, R. Tiruvalam, M. M. Forde, K. Sharples, A. Thetford, R. L. Jenkins, N. Dimitratos, J. A. Lopez-Sanchez, D. M. Murphy, D. Bethell, D. J. Willock, S. H. Taylor, D. W. Knight, C. J. Kiely and G. J. Hutchings, *Angew. Chem., Int. Ed.*, 2012, **51**, 5981–5985.
- 38 L. Kesavan, R. Tiruvalam, M. H. A. Rahim, M. I. bin Saiman, D. I. Enache, R. L. Jenkins, N. Dimitratos, J. A. Lopez-Sanchez, S. H. Taylor, D. W. Knight, C. J. Kiely and G. J. Hutchings, *Science*, 2011, **331**, 195–199.
- 39 J. A. Lopez-Sanchez, N. Dimitratos, P. Miedziak, E. Ntanjua, J. K. Edwards, D. Morgan, A. F. Carley, R. Tiruvalam, C. J. Kiely and G. J. Hutchings, *Phys. Chem. Chem. Phys.*, 2008, **10**, 1921–1930.
- 40 A. Thetford, G. J. Hutchings, S. H. Taylor and D. J. Willock, *Proc. R. Soc. A*, 2011, **467**, 1885–1899.
- 41 M. W. Lehenmeier, C. Bruckmeier, S. Klaus, J. E. Dengler, P. Deglmann, A.-K. Ott and B. Rieger, *Chem.-Eur. J.*, 2011, **17**, 8858–8869.