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Citation for final published version:

Pattisson, Samuel, Rogers, Owen, Whiston, Keith, Taylor, Stuart H. and Hutchings, Graham J. 2020. Low temperature solvent-free allylic oxidation of cyclohexene using graphitic oxide catalysts. *Catalysis Today* 357 , pp. 3-7. 10.1016/j.cattod.2019.04.053

Publishers page: <http://dx.doi.org/10.1016/j.cattod.2019.04.053>

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Low temperature solvent-free allylic oxidation of cyclohexene using graphitic oxide catalysts

Samuel Pattisson^{1,*}, Owen Rogers¹, Keith Whiston², Stuart H. Taylor¹, and Graham J. Hutchings^{1,*}

1 Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK.

2 INVISTA Performance Technologies, The Wilton Centre, Wilton, Redcar, TS10 4RF, United Kingdom.

* Correspondence: PattissonSD@cardiff.ac.uk Tel.: +44 2920 874061, Hutch@cardiff.ac.uk Tel.: +44 2920 874059

Abstract

A range of graphitic oxides have been utilised as metal free carbocatalysts for the low temperature oxidation of cyclohexene. The activity of the catalysts was correlated with the amount of surface oxygen on the graphitic oxide. In the case of cyclohexene oxidation, major selectivity is observed to allylic oxidation products. This is in contrast to the epoxide being the major product in linear alkene oxidation. This selectivity was maintained over long reaction times and at a conversion of above 50 %. Only small amounts of epoxide were observed, which eventually decreases at higher conversion due to hydrolysis to cyclohexane diol. The similarity between the non-catalysed and the catalysed product distribution suggests that these catalysts act as a solid initiator, and the role of the graphitic oxide is to decrease the lengthy induction period observed in the blank non-catalysed reaction.

Keywords: Cyclohexene, Carbocatalysis, Oxidation, Metal-free, Allylic

1. Introduction

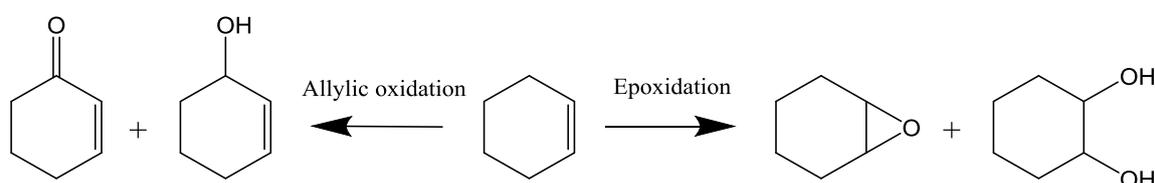
The selective oxidation of cyclic and linear alkenes is of great academic and industrial interest due to a variety of useful products being attainable through both direct oxidation of the carbon carbon double bond and allylic oxidation. However, these reactions are commonly conducted using expensive and stoichiometric oxidants[1] or require the use of initiators and metal catalysts for utilisation of oxygen as oxidant[2]. Over the past decade, the study of metal-free carbocatalysts has become increasingly popular[3]. Originally studied as intermediates in the chemical oxidation pathway for the synthesis of graphene[4], materials such as graphitic oxide, graphene oxide and reduced graphene oxide have seen a flurry of interest in catalytic applications due to their abundance of active oxygen functionality, surface defects and high degree of tailoring for a given reaction[5,6].

Previously, we have found that graphitic oxide (GO) is active for the initiator-free and solvent-free, low temperature oxidation of a range of linear alkenes[7]. The activity of these catalysts was found to be highly sensitive to the amount and type of oxidant used in the preparation, with the conventional Hummers (HU) based materials[8] being far from optimum. The major product was found to be the epoxide, which reached a maximum selectivity of *ca.* 45 %. The use of carbocatalysts for the oxidation of cyclic alkenes has been studied[9], however, these are commonly conducted at higher temperatures where an appreciable uncatalysed autoxidation reaction is observed, and within specific solvents in order to maximise activity and selectivity[10].

In this study we have investigated the use of a similar range of GOs to investigate their efficacy for the low temperature solventless oxidation of cyclohexene. This particular reaction is of great interest due to a number of its products being valuable intermediates in both synthesis and industrial applications. The direct oxidation of the double bond yields cyclohexene epoxide which has uses in forming polymers and plastics. Importantly, the highly selective epoxidation of cyclohexene offers a potential alternative route for production of adipic acid, through cyclohexane diol and sequential aerobic oxidation steps. This route has recently become economically viable due to the improvements made in the partial hydrogenation of benzene through the Asahi process[11]. Through the use of air as the oxidant cyclohexene therefore offers a more atom economic and environmentally friendly route to the current oxidation of cyclohexane which uses nitric acid. The cyclohexene route has previously been successfully studied by Sato *et al.* who utilised hydrogen peroxide as oxidant in a biphasic system to obtain high yields of adipic acid[12]. Subsequent studies have focussed on the removal of toxic phase transfer agents, use of a single phase and heterogenisation of the catalyst. However, this route is ultimately limited by the uneconomic use of hydrogen peroxide. Solventless oxidation of cyclohexene utilising oxygen as the oxidant is an attractive prospect, however, this process is also limited due to the presence of an alternative allylic oxidation route (Scheme 1). Recent studies have shown the effectiveness of a tungsten oxide co-catalyst to direct the hydroperoxide intermediate towards the

epoxide, however, this is also limited due to the equimolar formation of the allylic alcohol[13]. The formation of cyclohexane diol is also restricted by the lack of water to facilitate hydrolysis of the epoxide[14].

Allylic oxidation of cyclohexene yields 2-cyclohexen-1-one and 2-cyclohexene-1-ol, both of which represent important fragrance molecules[15,16] and are important intermediates for the synthesis of pharmaceuticals, pesticides and insect pheromones[17]. The presence of reactive carbonyl groups are useful for organic synthesis, which lends itself to cycloaddition reactions[18]. Allylic oxidation reactions are generally performed using metal catalysts such as those based on Pd, Rh, Fe, Cu or Co[19–22]. However, these systems require the use of environmentally unfriendly oxidants such as PhIO, NaClO, and tBuOOH to achieve a catalytic turnover[23–28]. Achieving this reaction with molecular oxygen would be the ideal situation, but these reactions are limited in selectivity, reaction scope and in safety.[29] Allylic oxidation is favoured under autoxidation conditions due to the formation of an alkenyl hydroperoxide species, which can break down *via* a Russell termination to produce both allylic alcohol and ketone[15]. Catalysts may either be employed under these conditions to accelerate the selective breakdown of this peroxy intermediate to the allylic species, or to enable lower temperatures to be utilised. However, this commonly requires the use of initiators for aerobic oxidation or the use of stoichiometric oxidants such as tert-butyl hydroperoxide[30].



Scheme 1 Allylic oxidation and epoxidation of cyclohexene

In this study it was found that the low temperature, solventless oxidation of cyclohexene is achievable using graphitic oxide as a metal-free carbocatalyst.

2. Materials and methods

Graphite (<20 μm), nitric acid, potassium permanganate (97 %), potassium chlorate (99 %), n-decane (99 %), cyclohexene (99 %, inhibitor-free), 2-cyclohexen-1-ol (95 %), 2-cyclohexen-1-one (98 %) and cyclohexene oxide (98 %), hydrogen peroxide (30 % in water) were purchased from Sigma-Aldrich. sulfuric acid (95-98 %) and nitric acid (70 %) were purchased from Fisher scientific.

2.1 Preparation of Graphitic oxides

GO was prepared from graphite, according to the reported HO method[31]. Graphite (<20 μm , Sigma-Aldrich) was added to a mixture of concentrated sulfuric (75 ml) and nitric acid (25 ml), which was allowed to cool to 10 $^{\circ}\text{C}$ in an ice bath. Potassium chlorate (1–55 g) was added stepwise to the mixture

over a period of 30 min with vigorous stirring. Stirring was continued for 14 h after which the mixture was left in air for 96 h, followed by repeated decantation and centrifugation of the remaining GO material.

GO was prepared according to previously reported HU method[8] using graphite (<20 µm) as a precursor. Graphite (5 g) was added to a mixture of concentrated sulfuric (87.5 ml) and nitric acid (27.5 ml) under vigorous stirring. The mixture was allowed to cool to 10 °C in an ice bath. Potassium permanganate (15 g) was then added stepwise over a period of 2 h. The mixture was then allowed to reach room temperature over a period of 4 h, followed by heating to 35 °C for 30 min. Deionized water (250 ml) was added, causing the temperature to rise to 70 °C. A further portion of deionized water (1 l) was added, followed by addition of 3% H₂O₂ for the removal of any residual potassium permanganate. The mixture was allowed to settle overnight after which the GO was separated and washed repeatedly *via* centrifugation.

Centrifugation was conducted (14,000 rpm, 30 min, 20 °C) using a Beckman coulter centrifuge, JLA.16.250 rotor. Samples were dispersed in deionized water (200 ml) before centrifugation. This was repeated until a neutral pH was obtained after which the final supernatant was decanted and the retained HU and HO samples were dried in a vacuum (20 °C) or a regular oven (110 °C), respectively.

2.2 Oxidation of cyclohexene

Cyclohexene oxidation was performed in a Colaver reactor heated using an oil bath. The reactor was flushed with oxygen and remained connected to an O₂ delivery line throughout the reaction. Typically, a mixture of cyclohexene (10 mL), catalyst (0.1 g) and n-decane (1 mL, as an internal standard) was magnetically stirred (900rpm) at 60 °C for the required reaction time. After the reaction, the mixture was separated from the solid catalyst by centrifugation and prepared for analysis. The liquid samples were analysed *via* gas chromatography (GC). Quantification of conversion and selectivity was conducted using n-decane as an internal standard. Products were initially identified using GC-MS and later confirmed and calibrated against commercial standards. Gaseous products were not analysed due to the use of a Colaver reactor, however based on similar reactions conducted in other reactors this contribution is likely to be negligible.

3. Results and discussion

A selection of the previously studied graphitic oxides were employed in this study. The materials were chosen to represent various levels of oxidation and also the two main methods of oxidation: Hofmann and Hummers. Table 1 lists the chosen range and details the amount and type of oxidant used, with the obtained oxygen wt.%. The GO's were named (GO-XX##) according to whether the Hofmann (HO) or Hummers (HU) method utilised and also to signify the amount of oxidant (g) used per 5 g of graphite.

It is important to note that the level of surface oxidation does not scale linearly with the amount of oxidant used in preparation and therefore it is more optimal to consider catalyst activity as a function of oxygen wt.%. The full characterisation of these materials by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Thermo-gravimetric analysis (TGA) and TGA coupled mass spectrometry (TGA-MS) can be found in our previous work[7]. The range of GOs were initially tested for the oxidation of cyclohexene using mild reaction conditions (figure 1), in order to maximise the effect of the catalyst and minimise the contribution due to autoxidation. As observed with the oxidation of linear alkenes, the activity of the catalysts can be correlated with the amount of surface oxygen, with an optimum of 25 wt% being apparent for maximum catalyst activity (figure 1a). Each material is decorated with a range of functional groups which arise from the chemical oxidation of graphite. These include hydroxyl, epoxides, and carboxylic acids as the major functional groups however many more are common. No obvious benefit of conversion or selectivity is observed by increasing the oxidation of the surface, as demonstrated with the standard HU material at *ca.* 33 wt% oxygen. Furthermore, the selectivity across the range of GOs is unchanged, with major selectivity being to the allylic products, 2-cyclohexen-1-one and 2-cyclohexene-1-ol (figure 1b). Our previous work on linear alkene oxidation demonstrated that the selectivity profile as a function of conversion is reproducible across a range of alkenes, with high initial selectivity being observed to allylic products, which then diminishes to give epoxide as the major product[32]. The selectivity to epoxide is subsequently observed to decrease due to hydrolysis to the diol as a result of water formed *in situ*. The ring size of cyclic alkenes has previously been shown to heavily influence selectivity, with C₆ and below showing high selectivity to allylic products[33]. Alkenes of C₇ and above showed high selectivity to the epoxide. This was suggested to be a result of the associated energy for ring closure in a radical intermediate being greater for smaller ring sizes, as calculated by DFT. In the present study, the low selectivity to epoxide is likely to be due to the effect of ring size, as before the GO catalyst was found to be selective for epoxidation in octene, decene and dodecene oxidation[7].

In order to study the selectivity at higher conversions, the most active catalyst containing *ca.* 25 wt% oxygen (GO-HO30) was subjected to a time online study, with a blank reaction as a comparison (figure 2a). Interestingly, conversion in the blank reaction was found to increase dramatically after a long induction period of approximately 40 h. The catalysed reaction was found to reach higher conversions much earlier, with the modest differences seen over the first 24 h becoming more pronounced over the subsequent 24 h. The two reactions can then be observed to converge in terms of conversion with the catalysed reaction being similar to the blank over the total 72 h reaction period, where presumably the reaction becomes limited due to diffusion of reactants and formation of a biphasic mixture, as observed previously. This limit in conversion is unlikely to be due to deactivation of the catalyst through loss of oxygen, as the amount of oxygenated products is found to be far in excess of that which would result from a stoichiometric reaction with surface oxygen species. The selectivity profile observed in figure

2b demonstrates that even over long reaction times, and at high conversions, the selectivity to the allylic products is maintained. Only a small increase in the epoxide is observed, which eventually decreases as hydrolysis to the diol is promoted due to the presence of the water that is formed *in situ* in the reaction. The selectivity profile for the blank and catalysed reaction appears to be similar, with only small differences in total allylic selectivity over shorter reaction times. This allylic selectivity steadily decreases as the reaction proceeds, however, no increase in any other known product is observed indicating the formation of unidentified species. Interestingly, a plot of conversion against selectivity (figure 3) demonstrates that the catalysed and uncatalysed reaction follow almost identical selectivity profiles for allylic products. This suggests that the GO carbocatalyst has no effect on selectivity and is acting more as an initiator to decrease the lengthy induction period associated with the build-up of peroxy species in the uncatalysed reaction. Previous work by Dhakshinamoorthy *et al* studying the use of doped graphenes for the oxidation of benzylic hydrocarbons suggested that surface peroxy species are important in the propagation of radical mechanisms. The use of FT-Raman demonstrated that surface peroxy species were indeed present when the samples were heated to 100 °C in O₂, which then disappear when the atmosphere was switched to nitrogen. We suggest that the materials in the present study are behaving in a similar manner for the initiation of radical species and oxidation of linear alkenes. A recent study on cyclohexane oxidation has also highlighted the importance of surface oxygen groups for the propagation of a radical mechanism[34]. The researchers correlated activity with carboxylic acid content and size of the nano-graphene sheets. It was suggested that the carboxylic acid groups were responsible for the generation of superoxide ($\bullet\text{O}_2^-$) radicals, which aligned with previous studies utilising carbon nanotubes in the same reaction[35]. In the current study, as well as in the previous study on linear alkenes, it is observed that there is a poor correlation between carboxylic acid content and activity. Indeed, the Hummers materials are far from optimum catalytically despite containing the highest amount of carboxylic acid groups, as observed by XPS[7], suggesting that a different functional group may be responsible for the activity we observe. This oxygen containing functional group is likely to be of epoxy or hydroxyl type rather than higher oxidation products, such as a carboxylic acid moiety, due to the poor correlation with the amount of oxidant used (figure 1).

The steady decrease of the selectivity to allylic products over longer reaction times is evidently not due to the formation of any other known species, such as epoxide or diol. Instead, the decrease of selectivity is due to the formation of higher molecular weight polymeric species, as observed in the previously studied uncatalysed oxidation of cyclohexene[36]. Here, the reaction mixture can be seen to become viscous and with an obvious formation of darker reaction products. This also results in the dramatic reduction in carbon mass balance in the analysis (figure 4). Once again, both the uncatalysed and catalysed reaction show identical profiles, suggesting this process is unaffected by the presence of the catalyst.

4. Conclusions

We have shown that graphitic oxide can be used as a metal-free carbocatalyst for the low temperature allylic oxidation of cyclohexene. The reaction takes place under solvent-free conditions using oxygen as the oxidant. The activity of the catalysts can be correlated with the amount of surface oxygen present as observed previously with linear alkenes. An optimum level of surface oxygen was again found to be 25 wt %, however, the differences observed in this study are less pronounced than those observed for the oxidation of linear alkenes. This is possibly due to the lower reaction temperature utilised and lower amount of surface peroxy formation, accompanied with the presence of a minor blank reaction at 60 °C. All the catalysts were selective towards allylic species, and this remained as the major product even at high conversions. The similarities in the selectivity profile for the uncatalysed and catalysed reaction suggest that the catalyst is not influencing selectivity and most likely acting as an initiator in order to reduce the lengthy induction period. The difference in conversion over time between the blank and catalysed reaction becomes clearer, with graphitic oxide achieving much higher conversions, presumably due to the initiation of a radical mechanism by surface oxygen species. High conversions result in the steady decrease of selectivity to allylic species due to the formation of high molecular weight polymeric species, as observed in previous oxidations of cyclohexene, and ultimately resulting in dramatically lower carbon mass balances. This is another example of the use of graphitic oxide as a metal-free carbocatalyst for important chemical transformations.

Funding: This research was funded by INVISTA and the EPSRC

Conflicts of Interest: The authors declare no conflict of interest.

Table 1 Range of graphitic oxides prepared by Hofmann and Hummers methods and the obtained oxygen wt %.

Catalyst	Oxidant used per 5 g Graphite. (g)	Oxygen wt. %
GO-HO1	1	9.0
GO-HO2	2	8.9
GO-HO4	4	14.6
GO-HO15	15	18.6
GO-HO20	20	21.1
GO-HO30	30	25.0
GO-HU15	15	33.2

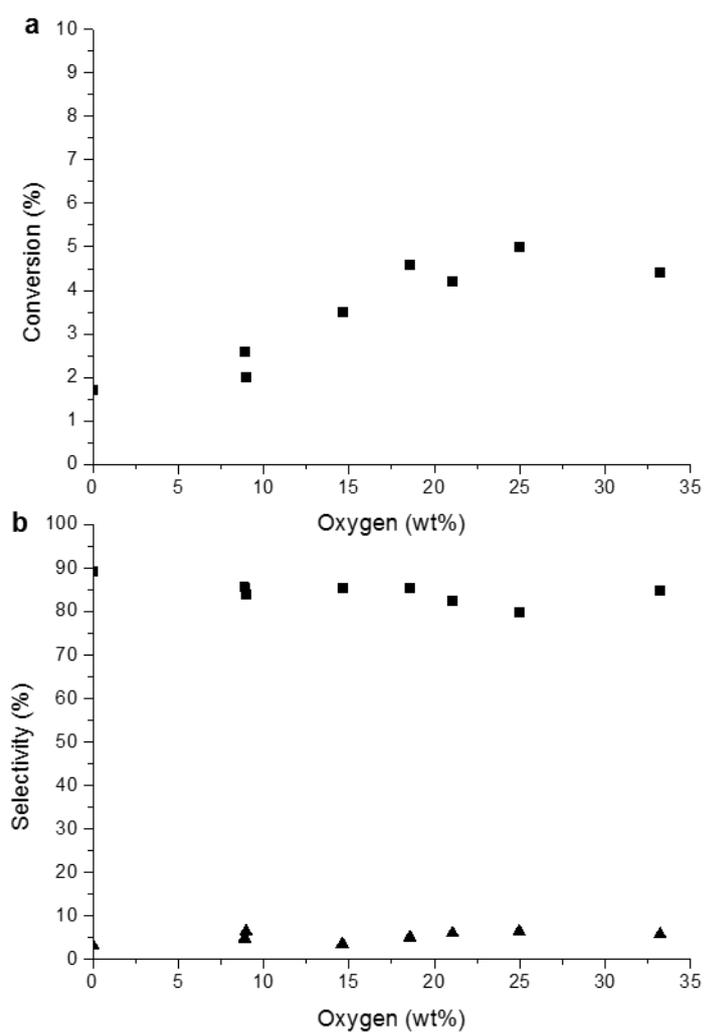


Figure 1 a) Catalytic activity of a range of graphitic oxides for cyclohexene oxidation and b) selectivity to cyclohexene oxide (▲) and combined allylic products (■) Conditions: catalyst (0.1 g), 24 h, 60 °C, cyclohexene (10 ml), decane (1 ml), O₂ (3 bar).

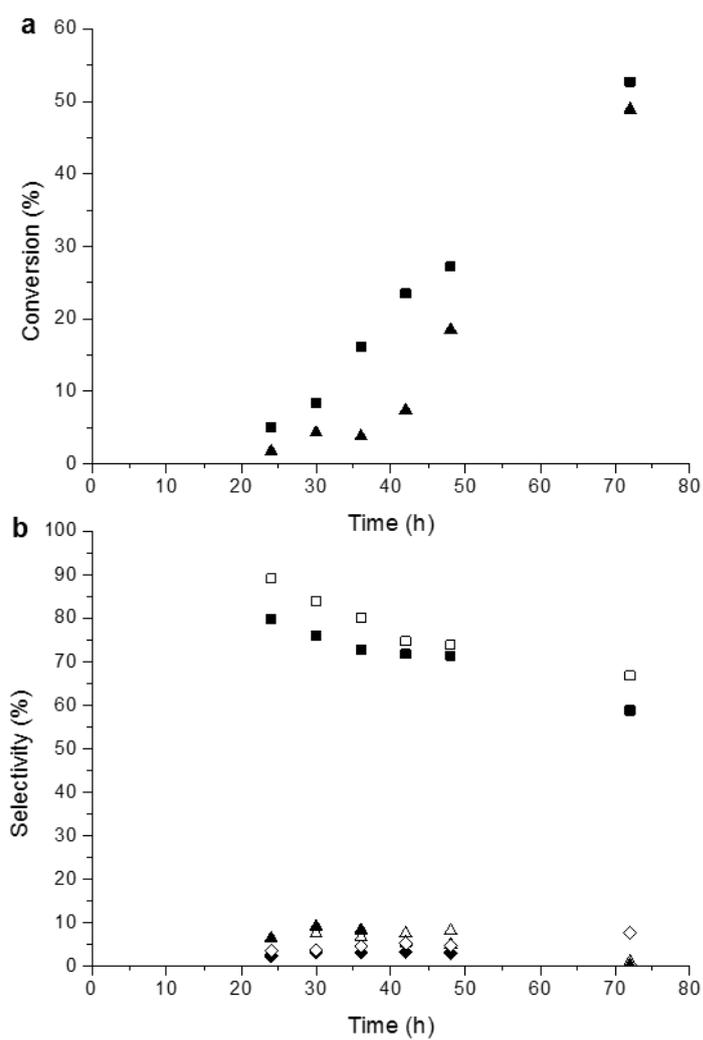


Figure 2 a) Time online comparison of GO-HO30 (■) and the blank reaction (▲) with b) their selectivities to cyclohexene oxide (▲), cyclohexane diol (◆) and total allylic products (■). GO-HO30 = closed symbols, blank reaction = open symbols. Conditions: catalyst (0.1 g), 60 °C, cyclohexene (10 ml), decane (1 ml), O₂ (3 bar).

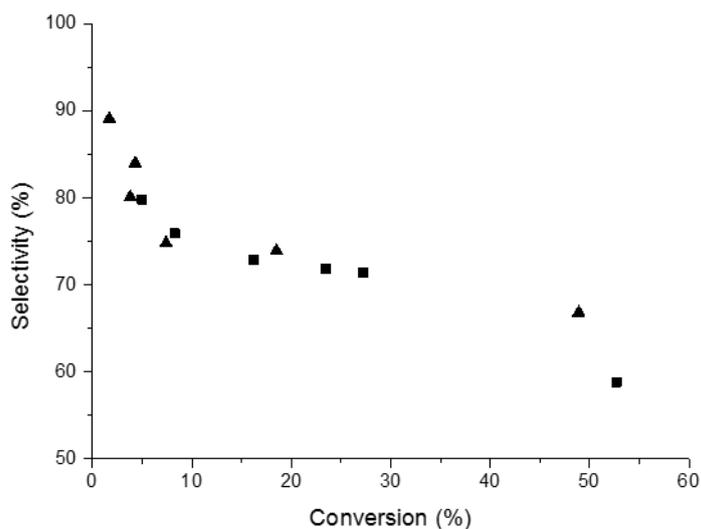


Figure 3 Conversion of cyclohexene versus selectivity to allylic products. Comparison for the GO-HO30 catalysed reaction (■) and the blank reaction (▲). Conditions: catalyst (0.1 g), 60 °C, cyclohexene (10 ml), decane (1 ml), O₂ (3 bar).

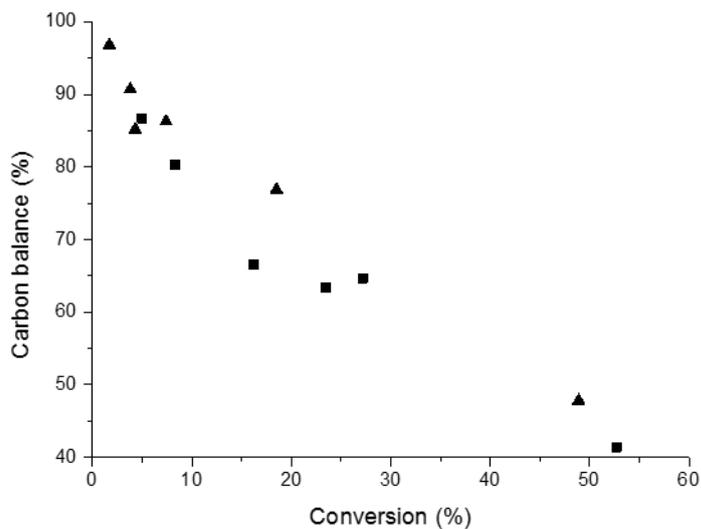


Figure 4 Conversion of cyclohexene versus carbon balance. Comparison for the GO-HO30 catalysed reaction (■) and the blank reaction (▲). Conditions: catalyst (0.1 g), 60 °C, cyclohexene (10 ml), decane (1 ml), O₂ (3 bar).

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