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Efficient green methanol synthesis from glycerol

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The production of biodiesel from the transesterification of plant-derived triglycerides with methanol has been commercialized extensively. Impure glycerol is obtained as a by-product at roughly one-tenth the mass of the biodiesel. Utilization of this crude glycerol is important in improving the viability of the overall process. Here we show that crude glycerol can be reacted with water over very simple basic or redox oxide catalysts to produce methanol in high yields, together with other useful chemicals, in a one-step low-pressure process. Our discovery opens up the possibility of recycling the crude glycerol produced during biodiesel manufacture. Furthermore, we show that molecules containing at least two hydroxyl groups can be converted into methanol, which demonstrates some aspects of the generality of this new chemistry.

There is presently a drive towards identifying new sustainable routes to important platform chemicals and fuels that can interface bioderived feedstocks[1–5] with current petrochemical and chemical industries that are based primarily on fossil fuels[6–8]. Much emphasis has been placed on biorefinery processes[9–11]. At present a number of processes have been developed and commercialized, including bioethanol and biobutanol as well as the production of biodiesel from the transesterification of plant-derived triglycerides with methanol[12–14]. This production of biodiesel produces impure glycerol as a by-product at roughly one-tenth the mass of the biodiesel[15] and consumes methanol derived from fossil fuels[16–18]. Utilization of this crude glycerol can present a problem for this technology and effectively is providing a brake on further development[19]. Pure refined glycerol is a high-value material with uses in pharmaceuticals and foodstuffs; however, at present crude glycerol from biodiesel production contains high levels of impurities that prevent its use in this form. Glycerol conversion by oxidation into glyceric acid[20], dehydration into acrolein[21–25] and hydrogenation into methanol[26,27] has been demonstrated, but to date only by using refined glycerol, which is an expensive and valuable material[28]. In this work we investigated a new reaction of glycerol with water using very simple basic or redox oxide catalysts to produce methanol in high yields, together with other useful chemicals, in a one-step low-pressure process. Our discovery opens up the possibility of recycling the crude glycerol produced during biodiesel manufacture and so provide a means to replace methanol derived from fossil fuel.

The conversion of glycerol has been the focus of extensive research as it is a highly functionalized molecule readily derived from biomass. One desirable target is to convert glycerol into methanol, which is a major chemical intermediate of immense utility. However, the central problem for the conversion of glycerol into methanol is that hydrogen has to be introduced, as demonstrated by Wu *et al.*[27], who hydrogenated glycerol with H_2. We wanted to explore the reactivity of glycerol using water as a potential hydrogen source specifically under conditions in which synthesis gas ($CO + H_2$) is not required as a key intermediate.

Results

Our initial experiments focused on extending our earlier studies concerning the acid-catalysed dehydration of glycerol into acrolein[21,25]. We considered that the dehydration reaction could also be base catalysed. On this basis we reacted aqueous glycerol (Supplementary Figs 1–3) over MgO, a well-known basic oxide, under reaction conditions similar to those we had used for acrolein formation catalysed by strong acids (that is, 500–600 K, 10% glycerol in water)[21,25]. In these initial exploratory experiments we used pure glycerol in line with previous experimental studies. We observed (Supplementary Table 1) that acrolein was still formed, but as a minor product. Surprisingly, we identified methanol as the major product (Fig. 1). Indeed, we had found methanol as a very minor product (about 1%) in the previously published acid-catalysed chemistry[21,25]. At a relatively low temperature (523 K) and with MgO, acrolein was observed with a selectivity of about 10% and methanol at about 30%. However, as the reaction temperature was increased the formation of acrolein diminished as the conversion continued and methanol became the dominant product (Supplementary Fig. 4 and Supplementary Table 1). With CaO, a stronger base, the formation of methanol was enhanced, although the overall conversion was decreased (Fig. 1). We then made a number of mixed magnesium/calcium oxides (Fig. 1 and Supplementary Table 1) by mixing freshly prepared MgO and CaO, and observed that these mixed oxides retained the high conversion levels associated with MgO, but exhibited a much higher selectivity than the separate oxides, which indicated the presence of a synergistic effect. SrO and mixed oxides of strontium and magnesium were not as effective (Fig. 1 and Supplementary Table 1). It is clear that a range of products was formed in addition to methanol. These included acetol and ethanal, and at low temperatures acrolein and ethylene glycol. Other products formed in low selectivities (<5%) were ethanol, propanal, 1-propanol, 2-propanol, allyl alcohol, 2,3-butanedione, 2-hexanone, acetone and CO_2. Acetol and acrolein are the products of dehydration. Further reduction of acrolein gives allyl alcohol and propanal; reduction of acetol gives acetone. However, the formation of methanol requires carbon–carbon bond scission and a source of hydrogen. Detailed isotopic labelling experiments were carried out to explore this new chemistry further. The presence of methanol was confirmed by using 1,2,3-^{13}C-*tris*-glycerol (Aldrich 99%), which resulted in ^{13}C-methanol identified by the presence of a doublet in the proton NMR spectrum centred at 3.3 ppm with a coupling constant of 142 Hz.

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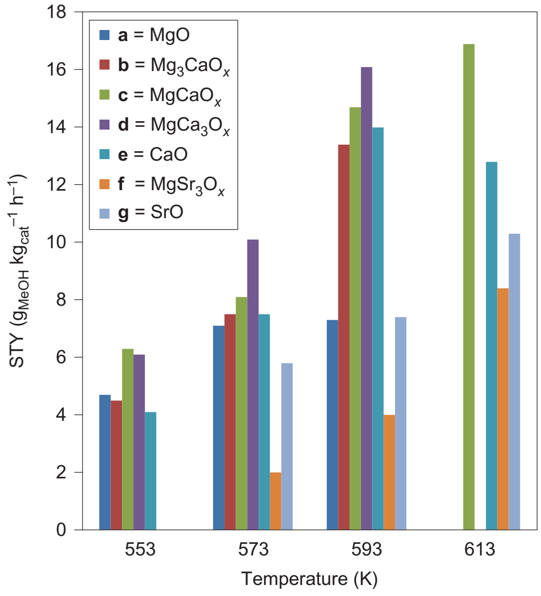

Figure 1 | Catalytic activity of the metal-oxide and mixed metal-oxide materials. a–g, Space-time yield (STY) is defined as the grams of methanol produced per kilogram of catalyst per hour, and is presented as a function of the reaction temperature. The activity of the catalysts generally increases with increasing temperature. **a**, Over MgO, BET surface area 144 m^2 g^{-1}. **b**, Mg_3CaO_x, 25 m^2 g^{-1}. **c**, $MgCaO_x$, 17 m^2 g^{-1}. **d**, $MgCa_3O_x$, 11 m^2 g^{-1}. **e**, CaO, 13 m^2 g^{-1}. **f**, $MgSr_3O_x$, 3 m^2 g^{-1}. **g**, SrO, 3 m^2 g^{-1}. The experiments were carried out in a stainless-steel fixed-bed flow reactor housed in a furnace for temperature control. Experiments were performed under the following conditions: catalyst (0.5 g), feed flow (1 ml h^{-1}, 10 wt% glycerol/H_2O), inert carrier (100 ml min^{-1}), three hours. Full reaction data concerning the conversion and selectivity are given in Supplementary Table 1.

Reactions with $H_2{}^{18}O$ did not lead to the formation of ^{18}O-methanol (Supplementary Figs 5 and 6). The use of D_2O led to a 50% decrease in the glycerol conversion, which indicates the presence of a significant isotope effect. On the basis of these results we concluded that water was acting as a source of the hydrogen required for methanol formation in this reductive process.

We investigated the method of MgO preparation to determine whether better catalysts could be obtained. We made a series of four magnesium oxides using different heat treatments (Supplementary Fig. 4) and observed that for each of these the product selectivities were almost identical, but the activities were related directly to the surface area of the MgO (Supplementary Fig. 4), which indicates that an important aspect of catalyst design is to maximize the surface area. With the most active of these MgO samples (denoted MgO (**A**), see Supplementary Fig. 4), we then investigated higher concentrations of glycerol. We found we could achieve similar conversions with higher concentrations of glycerol (up to 30%) by increasing the catalyst mass, and that the conversion could typically be maintained at about 25% with 40% methanol selectivity (Supplementary Fig. 7). Extending the reaction time to 35 hours showed no loss of activity or selectivity and the catalyst performance was stable over this period (Supplementary Fig. 7).

In the next set of experiments we used lanthanide-based oxides (Supplementary Table 2) and were pleased to find that CeO_2, a reducible oxide, was very effective. This suggests that a wide range of oxide catalysts may be effective catalysts for this new chemistry. With MgO (Fig. 1 and Supplementary Table 1) we found that conversions were typically about 25% and we could not significantly improve on this. However, with CeO_2 and by either increasing the temperature or increasing the catalyst mass, we could achieve complete glycerol conversion and increase the methanol selectivity to 60% (Fig. 2).

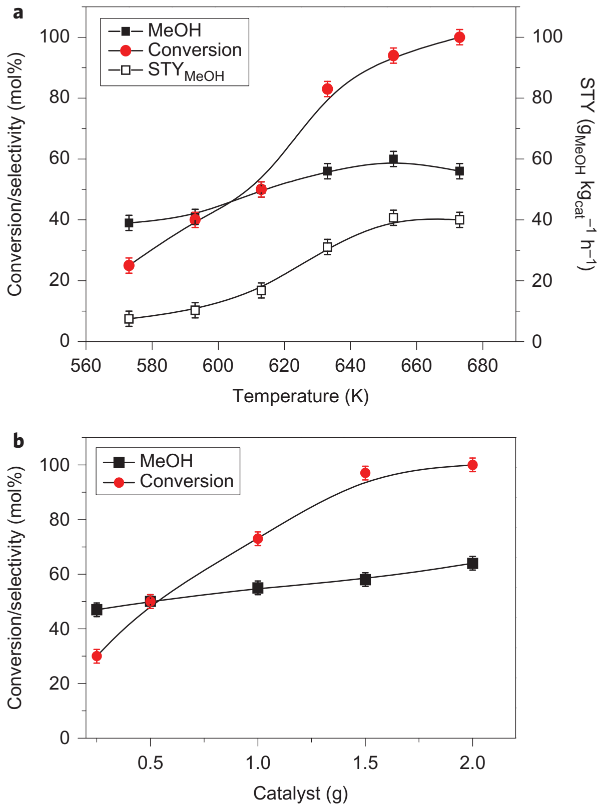

Figure 2 | Catalytic conversion of glycerol over cerium oxide and selectivity to methanol. a, Effect of temperature on the conversion (mol%) of glycerol (10 wt%) and methanol selectivity (mol%), which indicates that the space–time yield (STY) of methanol reaches a plateau with increasing temperature. Experimental conditions: 0.5 g catalyst, 100 ml min^{-1} inert carrier, 1 ml h^{-1} feed flow, products collected for three hours. **b**, Influence of contact time on glycerol conversion (mol%) and methanol selectivity (mol%) at 613 K suggests that the MeOH selectivity can improve with increased contact time. Experimental conditions: 100 ml min^{-1} inert carrier, 1 ml h^{-1} feed flow, products collected for three hours. Experimental error is ±5% as represented by the error bars.

We investigated the reaction of other oxygenates over MgO as a catalyst. Methanol was formed from ethylene glycol and 1,3-propanediol (Fig. 3), but not from 1- or 2-propanol. It is apparent that molecules require more than one hydroxyl group for this reaction to be observed. In this initial stage of the study we have not explored fully the potential range of substrates from which methanol can be formed.

To deduce the possible reaction pathways by which methanol is formed, both over MgO, a non-reducible basic oxide, and over CeO_2, a reducible oxide, we reacted separately the observed products over these catalysts. Methanol, ethanol, acetone, 1- and 2-propanol and acrolein proved unreactive, which indicates these to be terminal products. We consider that both thermal dehydration and radical fragmentation in a reductive atmosphere, which would be present in steam at this temperature[29], would dominate this degradation of glycerol **1** (Fig. 4). Double dehydration under these basic conditions generates a relatively small amount of acrolein (**2**), which becomes lower at higher temperatures, in contrast to the related acid-catalysed reaction. The major pathway appears to feature monodehydration with the loss of a terminal hydroxyl and the formation of enol **3**, tautomeric with acetol (**4**), followed by radical fragmentation related to a Norrish type-1 process to give the methanol precursor **5** and the acetyl radical **6**; subsequent reduction leads to methanol and ethanal

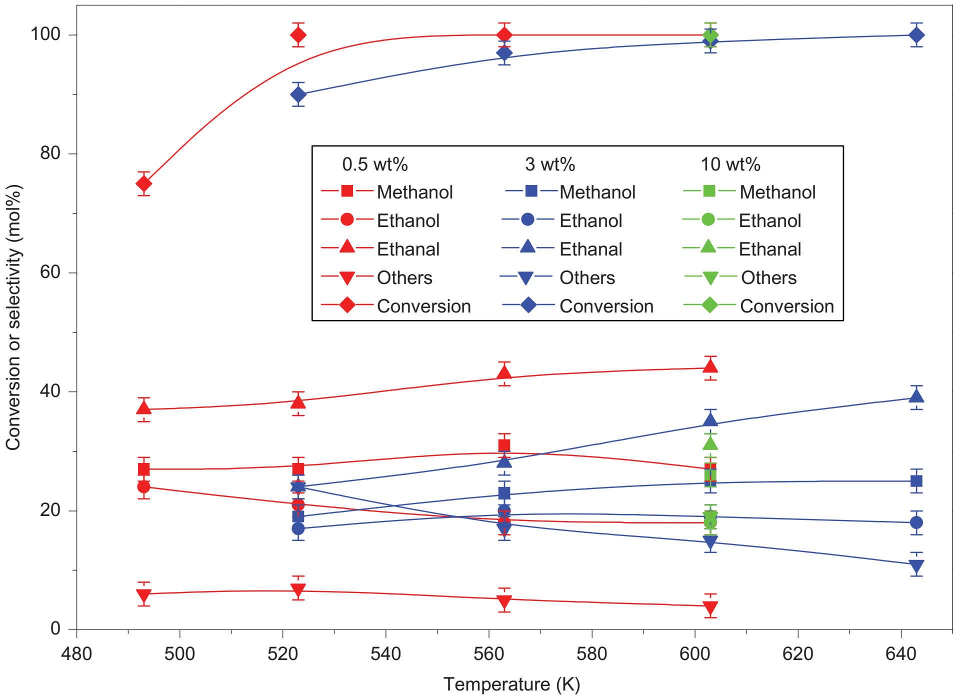

Figure 3 | The influence of reaction temperature on the conversion and product selectivities (mol%) over MgO (A) with different feed concentrations of 1,3-propanediol. The formation of methanol requires a reactant with at least two hydroxyl groups as no products were detected with 1- or 2-propanol. Reaction conditions: 1 ml h^{-1} feed flow, 100 ml min^{-1} inert carrier, 0.25 g catalyst (0.5 g for 10 wt% feed) for three hours. 'Others' represents a combination of acrolein, propionaldehyde, allyl alcohol and 1-propanol in mol%. Experimental error is ±5% as represented by the error bars.

(**7**), respectively. Further reduction of the latter could account for the formation of ethanol (**9**); arguably, the unlikely formation of 2,3-butanedione (**8**) provides strong support for the intermediacy of the acetyl radical **6**.

We regard a second pathway, initiated by a C–C bond cleavage, as minor when using MgO. Such a reaction would generate the same methanol precursor **5**, together with the ethylene glycol radical **10**, which could lose a hydrogen radical to give enediol (**11**) and thence hydroxyethanal (**12**), fragmentation of which, again by a Norrish type-1 process, would give more of the methanol radical **5** and formaldehyde precursor **13**, which could also be reduced to methanol. When carried out over ceria there is a distinct increase in the formation of products derived from the latter pathway, mostly methanol from at least two reactions, at the expense of those (**7** and **8**) derived from the major route. It is unclear which factor determines this change—either greater initial C–C bond cleavage (to give **5** and **10**) or a slowing of monodehydration that leads to acetol (**4**).

Until now we had been using refined glycerol, which is a premium product and does not represent a viable economic starting point for methanol synthesis. Glycerol is formed as a by-product of biodiesel production, in which fatty triglycerides, derived from vegetable oils, tallow and even waste from the food industry, are transesterified using methanol. Crude glycerol contains many impurities, including traces of NaOH (the catalyst used in its manufacture), unreacted or partly reacted triglycerides, nitrogenous compounds of plant origin and long-chain acids and long-chain alkanes. In our final set of experiments we used crude glycerol from a biodiesel plant (Biodiesel Amsterdam BV). The crude glycerol contained two phases, namely, aqueous glycerol in one phase and a minor component of unreacted triglycerides and other organic material present in a separate phase (Supplementary Figs 8 and 9). We separated the aqueous glycerol layer from the organic layer and then treated the aqueous layer with activated carbon (Supplementary Fig. 10). After this simple treatment, the crude glycerol was reacted with CeO_2. The results (Fig. 5 and Supplementary Table 3) show that we obtained very similar outcomes using this crude material as those using refined glycerol (Fig. 5).

Discussion

We consider that the initial potential exploitation of the new chemistry we have identified is in the fatty acid methyl ester (FAME)-based biodiesel industry, which is the source of the crude glycerol. Although the availability of glycerol as a by-product is rather stable for the time being, we consider that there remains an opportunity to optimize the overall production of biodiesel by incorporating biomethanol based on our new chemistry into the FAME product, and thereby make better use of the vegetable oil feedstock. In FAME, the methanol only accounts for a small percentage of the product molecule (about 11%), and is limited to about 7% in the diesel blend. There is, therefore, significant value in increasing the efficiency with which we use crop-based feedstocks, and increasing the renewable content of the biofuels derived from them. Using renewable methanol to make FAME enables around a 10% increase in its renewable content, which could be very helpful to the industry at this time. It is certainly true that there are alternative uses for glycerol in the production of higher-value chemicals, and it is also probable that methanol derived from glycerol will not be cost competitive with methanol derived from natural gas. However, we do not anticipate that the new chemistry will find its initial application outside the biodiesel arena and we anticipate that the new process will permit 100% renewable FAME to be produced rather than 90% renewable FAME. As to the likelihood of its development, our process has several benefits. First, the process design is very simple and the conditions are mild. Second, the methanol produced can be used directly in the transalkylation process for the production of FAME. It is always a very favourable situation when stoichiometric amounts of chemicals needed in a process are prepared on-site.

It is also important to consider competing uses for crude glycerol. Recently, the integration of glycerol conversion into syngas

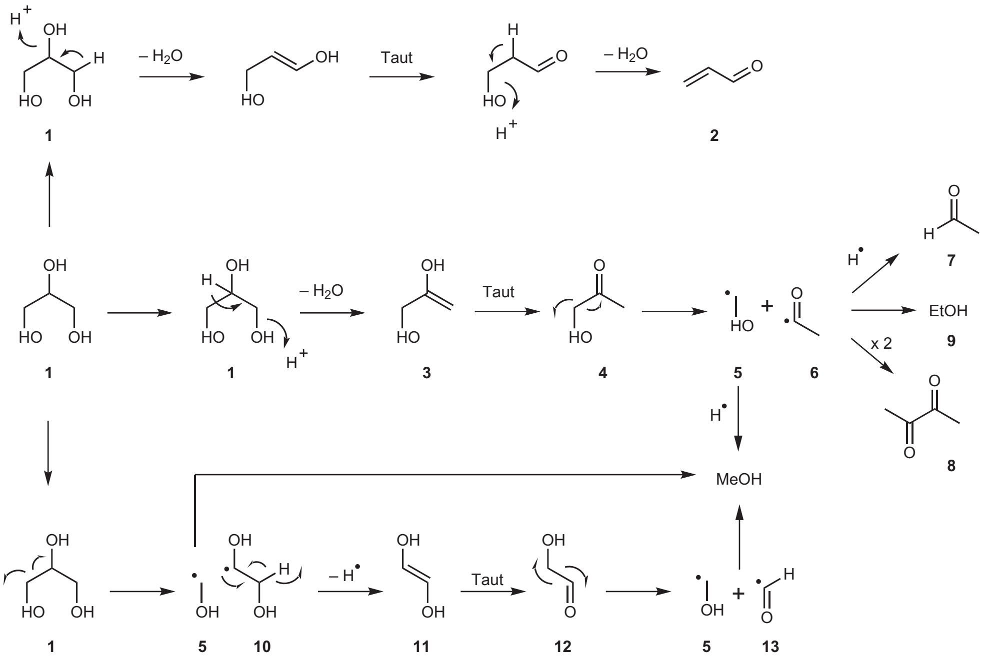

Figure 4 | Proposed mechanism for the formation of methanol from glycerol (1). Over base catalysts glycerol can undergo dehydration to form reactive species, which results in the production of methanol as the major product and of other secondary products, such as acrolein (**2**), 2,3-butanedione (**8**) and ethanol (**9**). Taut, enol–keto tautomerism.

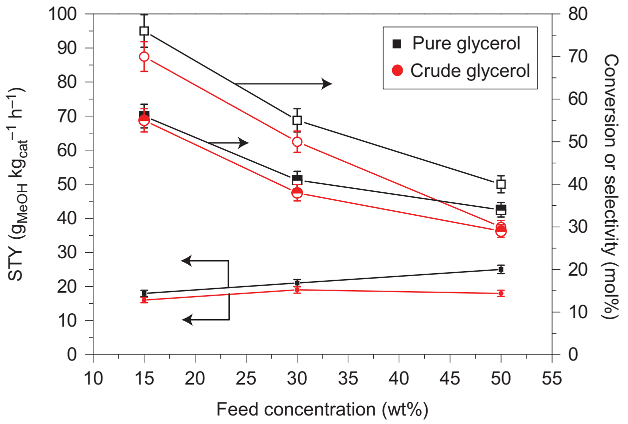

Figure 5 | Catalytic activity of CeO_2 increases the glycerol feed concentration for both pure and crude glycerol. The pure glycerol solutions were prepared by diluting glycerol (99.9%) with water, whereas the crude glycerol solutions were prepared by diluting crude glycerol (about 85 wt% in water). The catalyst is tolerant of impurities in the feed stream in the case of the reactions with crude glycerol; however, over three hours the conversion is lower than that with the corresponding pure solutions. Glycerol conversion is represented by open symbols and methanol selectivity by half-filled symbols. Reaction conditions: 1.0 g ceria, 1 ml h^{-1} feed flow, 100 ml min^{-1} inert carrier, three hours duration at 613 K. Experimental error is ±5% as represented by error bars.

coupled with the production of the resultant methanol has been studied. This study, referred to as the Supermethanol concept, is a good benchmark with which to compare our new chemistry. In the Supermethanol process several chemical conversions are needed that involve harsh conditions: the reforming reaction (24–27 MPa, 950–1,000 K) and the methanol synthesis reaction (24–27 MPa, 470–520 K) and, in addition, reactions and separations are needed to tune the CO/CO_2 ratio to the right value. Compared to this process, our process is remarkably simple. Only one chemical conversion step is needed and the conditions are mild at 523–680 K and atmospheric pressure. The reaction is based on heterogeneous catalysis in the gas phase. A simple process design (single-phase fixed-bed reactor, and easy product separation by distillation) is possible. Indeed, the separation of methanol from crude glycerol by distillation is common practice in existing biodiesel plants. Of course, catalyst development work has to be done to optimize the catalyst, and this has yet to be carried out. In particular, catalyst stability, often negatively influenced by real feedstocks, is crucial for a satisfactory practical process. Our exploratory study shows promising results: stable catalyst performance of over more than a day and impurities in the crude glycerol do not cause large problems with catalyst stability.

Therefore, we consider that our results pave the way for a new catalytic route from aqueous glycerol to methanol, to be used to recycle crude glycerol as methanol in a biodiesel production unit. We have not attempted to optimize the catalyst design and there is no doubt immense scope to generate catalysts with enhanced activity and selectivity. However, we have shown that methanol can be produced in a new catalytic reaction that requires neither high pressure nor hydrogen.

Methods

The MgO (**A**) catalyst was prepared by first calcining high-purity hydroxide (99% Sigma Aldrich) at 723 K for 24 hours. The resulting solid was then sieved between 250 and 425 μm followed by refluxing in water (15 ml g^{-1} for three hours). The resulting slurry was dried at 383 K for 24 hours and then heated at 875 K under flowing N_2 (100 ml min^{-1}) for three hours. A range of MgO catalysts (denoted (**B**)–(**D**)) was also prepared by varying the thermal treatment of the hydroxide precursor (Supplementary Information). The oxide catalysts of Ca, Sr, La and Ce were also prepared by the same procedure (without sieving) from their respective high-purity hydroxides (99%+ Aldrich). Mg/Ca mixed oxides were prepared by physically grinding different proportions of MgO (**A**) and CaO before pelleting and sieving (250–425 μm). Mixed metal-oxide catalysts of Mg/Sr were prepared by mixing the corresponding nitrate solutions (total molarity, 1 mol dm^{-3}) in an appropriate ratio. The solutions were heated to 343 K and aqueous ammonia was added to form a precipitate (pH = 9, 10), which was collected by evaporating to dryness, and the catalysts formed by heating at 1,073 K under flowing N_2 for three hours. Surface areas were determined according to the Brunauer–Emmett–Teller (BET) method.

Catalytic reactions were evaluated using a gas-phase plug flow microreactor (Supplementary Figs 10 and 11). The aqueous glycerol feed was introduced into a preheater and vaporizer (573 K) using an HPLC pump with a precisely controlled flow rate (0.017 ml min^{-1}). The vaporized feed was then swept through the reactor system in a flow of nitrogen carrier gas (100 ml min^{-1}). All of the catalysts were pressed and sieved to a uniform particle size (250–425 µm) before use, and were packed into an 8 mm inner diameter (i.d.) stainless-steel tube between plugs of silica wool. The catalysts were packed to a uniform volume of 0.25 to 5 cm^3, which permitted typical gas hourly space velocities of 2,000–24,000 h^{-1}. The catalyst bed was heated using an electric furnace placed around the reactor tube and the temperature of the catalyst was maintained using a proportional integral derivative temperature controller linked to a thermocouple placed in the catalyst bed. After exiting the catalyst bed the lines were trace heated to prevent any condensation taking place. Unreacted glycerol and the reaction products were collected for analysis in a series of cold traps. Three traps were used, as this was found to be the most efficient method and ensured that any carry-over from the first trap was collected subsequently. Crude glycerol was supplied by Biodiesel Amsterdam BV and treated by decantation of the aqueous phase followed by simple filtration through charcoal to remove coloured impurities.

Reaction products, collected in the cold traps, were combined for analysis, which was performed offline using a Varian CP 3800 gas chromatograph equipped with a capillary column (ZBWAX plus, i.d. 0.53×30 m). Gas samples were also collected and analysed off-line by means of a Varian CP 3800 GC with a Poropack Q 1/8″ × 2 m column. Product selectivities (mol%) were calculated from the moles of product recovered divided by the total moles of all products.

The liquid-phase products were analysed by ^{1}H NMR spectroscopy. NMR spectra were recorded at room temperature on a Bruker DPX 500 MHz Ultra-Shield NMR spectrometer (1H 500.13 MHz), and quantified with a 1% Me$_4$Si/CDCl$_3$ internal standard contained in a sealed glass ampoule, which was calibrated against a known concentration of methanol. Typically, 0.7 ml of sample and 0.1 ml of D$_2$O were placed in an NMR tube along with the internal standard. A solvent-suppression program was run to minimize the signal that arises from the water. Chemical shifts were reported in parts per million relative to Me$_4$Si. Formaldehyde was determined using HPLC. The liquid sample was drawn through a silica gel packed cartridge coated with 2,4-dinitrophenylhydrazine (DNPH). Any formaldehyde within the reaction solution readily forms a stable derivative with the DNPH reagent. The derivative was eluted from the column with acetonitrile and analysed by reverse-phase chromatography using a photodiode array detector set at 360 nm. The presence of formaldehyde was confirmed via the comparison of retention times with those of standard DNPH derivatives of this compound. Quantification of the formaldehyde DNPH derivative was achieved against a range of formaldehyde DNPH solutions of known concentration. Formaldehyde was detected only in trace quantities (parts per million).

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Author contributions

M.H.H. prepared and tested the catalysts and designed the initial experiments, N.F.D designed the reactor and provided assistance with experimental design and D.W.K. provided mechanistic insights into the chemistry. Detailed analysis was provided by R.L.J. S.H.T provided expertise on catalyst preparation. G.J.H. directed the overall research and all the authors contributed to the analysis of the data and the writing of the manuscript.

Additional information

All the data created during this research are openly available from the Cardiff University data archive at http://dx.doi.org/10.17035/d.2015.100110. Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to M.H.H. and G.J.H.

Competing financial interests

The authors declare no competing financial interests.