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Efficient green methanol synthesis from glycerol

Muhammad H. Haider[1,2]*, Nicholas F. Dummer[1], David W. Knight[1], Robert L. Jenkins[1], Mark Howard[3], Jacob Moulijn[1], Stuart H. Taylor[1] and Graham J. Hutchings[1]*

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

*Corresponding authors: mhhaider@yahoo.com, Hutch@cardiff.ac.uk

[1]Cardiff Catalysis Institute, School of Chemistry. Cardiff University, Cardiff, CF10 3AT

[2]Present address: Dr. Muhammad H. Haider, Sabic Technology & Innovation Center (STC), Riyadh11551 P.O. Box 42503

[3]Hull Research & Technology Centre, Saltend, Hull, HU12 8DS, UK

Abstract

The production of bio-diesel from the transesterification of plant-derived triglycerides with methanol has been extensively commercialised. Impure glycerol is obtained as a by-product at roughly one tenth the mass of bio-diesel. Utilisation 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 bio-diesel manufacture. Furthermore, we show that molecules containing at least two hydroxyl groups can be converted into methanol demonstrating aspects of generality of this new chemistry.

There is presently a drive towards identifying new sustainable routes to important platform chemicals and fuels that can interface bio-derived feedstocks[1-5] with the current petrochemical and chemical industries that are based primarily on fossil fuels[6,7]. Much emphasis has been placed on biorefinery processes[8-10]. At present a number of processes have been developed and commercialised including bio-ethanol and biobutanol as well as the production of bio-diesel from the transesterification of plant-derived triglycerides with methanol[11-13]. This production of biodiesel produces impure glycerol as a by-product at roughly one tenth the mass of bio-diesel[14] and consumes methanol derived from fossil fuels [15-18]. Utilisation 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 prevents it use in this form. Glycerol conversion by oxidation to glyceric acid[20], dehydration to acrolein[21-25] and hydrogenation to methanol[26,27] has been demonstrated but to date only using refined glycerol which as we note an expensive material and valuable material[28]. In the present work we have 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 bio-diesel manufacture providing a means to replace fossil fuel-derived methanol.

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 to methanol which is a major chemical intermediate which immense utility. However, the central problem for the conversion of glycerol to methanol is 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 where 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 to acrolein[21,25]. We considered that the dehydration reaction could also be base-catalysed. On this basis we reacted aqueous glycerol (see supplemental material Figures S1-S3) over MgO, a well-known basic oxide under reaction conditions similar to those we had used for acrolein formation catalysed by strong acids (i.e. 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 (Figure 1 and Supplementary Table S1) that acrolein was still formed but as a minor product. Surprisingly, we identified methanol as the major product. Indeed, we had found methanol as a very minor product (*ca.* 1%) in the previously published acid-catalysed chemistry[21,25]. At a relatively low temperature (523 K), with MgO acrolein is observed with a selectivity of *ca.* 10% and methanol at *ca.* 30%; but as the reaction temperature is increased so the formation of acrolein is diminished as the conversion increases and methanol becomes the dominant product (Supplementary Table S1, supplementary Figure S4). With CaO, a stronger base, (Figure 1) the formation of methanol is enhanced although the overall conversion is decreased. We then made a number of mixed magnesium/calcium oxides (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 much higher selectivity than the separate oxides indicating the presence of a synergistic effect. Use of SrO and mixed oxides of strontium and magnesium were not as effective (Fig. 1 and Supplementary Table S1). It is clear that a range of products are formed in addition to methanol. These include acetol and ethanal, and at low temperatures acrolein and ethylene glycol. Other products formed in low selectivities (<5%) are 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 and further reduction of acrolein and acetol will give allyl alcohol, propanal and acetone respectively. However, the formation of methanol requires carbon-carbon bond scission and a source of hydrogen. Detailed isotopic labeling 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. Reactions with $H_2{}^{18}O$ did not lead to the formation of ^{18}O-methanol (Supplemental Figure S5 and S6). The use of D_2O led to a 50% decrease in the glycerol conversion indicating the presence of a significant isotope effect. On the basis of these results we concluded that water was acting as a source of hydrogen that is required for methanol formation in this reductive process.

We investigated the method of MgO preparation to determine if improved catalysts could be obtained. We made a series of four magnesium oxides using different heat treatments (Supplementary Figure S4) and observed that for each of the product selectivities were almost identical but the activities were directly related to the surface area of the MgO (Supplementary Figure S4) indicating that an important aspect of catalyst design is maximizing the surface area. With the most active of these MgO samples (denoted MgO (**A**), see supplementary data Figure S4), 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 *ca.* 25% with 40% methanol selectivity (see supplementary material Figure S7). Extending the reaction time to 35 h showed no loss of activity or selectivity and the catalyst performance was stable over this period (see supplementary material Figure S7).

In the next set of experiments we used lanthanide-based oxides (Supplementary Table S2) 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 for catalysing this new chemistry. With MgO (Figure 1 and Supplementary Table S1) we found that conversions were typically *ca.* 25% and we could not significantly improve upon this. However, with CeO_2 by either increasing the temperature or increasing the catalyst mass, we could achieve complete glycerol conversion and increase the methanol selectivity to 60% (Figure 2).

We investigated the reaction of other oxygenates over MgO as a catalyst. Methanol is formed from ethylene glycol, 1,3-propanediol (Figure 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 fully explored the potential range of substrates from which methanol can be formed.

To deduce 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, indicating 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** (Figure 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 mono-dehydration with loss of a terminal hydroxyl and 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 **7** respectively. Further reduction of the latter could account for the formation of ethanol **9**; and 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 hydroxy-ethanal **12**, fragmentation of which, again by a Norrish type-1 process, would give more 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 products derived from the latter pathway, mostly methanol from at least two reactions, at the expense of those (**7** and **8**) 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 mono-dehydration leading 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 from 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 B.V). 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 (see supplementary data Figures S8 and S9). We separated the aqueous glycerol layer from the organic layer and then treated the aqueous layer with activated carbon (see supplementary data Figure S10). Following this simple treatment, the crude glycerol was reacted with CeO_2; the results

(Figure 5 and Supplementary Table S3) shows that we obtained very similar results using this crude material as those using refined glycerol (Figure 5).

Discussion

We consider that the new chemistry we have identified will have potential for initial exploitation 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 bio-methanol based on our new chemistry into the FAME product, thereby making better use of the vegetable oil feedstock. In FAME the methanol only accounts for a small percentage of the product molecule (*ca.* 11%). and is limited to *ca.* 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 and this could be very helpful to the industry at this time. It is certainly true that there are alternative uses for glycerol into higher value chemicals, and it is also probable that methanol derived from glycerol will not be cost competitive with methanol from natural gas. However, we do not anticipate that the new chemistry will find application initially outside the biodiesel arena and we anticipate that the new process will permit 100% renewable FAME to be produced rather than 90% renewable FAME. Regarding the likelihood of the development we note that our process has several benefits. First, the process design is very simple and the conditions are mild. Second, the methanol produced can be directly used 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 an integration of glycerol conversion to syngas coupled with the production of methanol produced 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, involving harsh conditions: reforming reaction (24-27 MPa, 950-1000 K), 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: 523-680 K; atmospheric pressure. The reaction is based on heterogeneous catalysis in the gas phase. A simple process design (single phase fixed bed reactor, easy product separation by distillation) is possible. In fact, the separation of methanol/crude glycerol by distillation is common practice in existing biodiesel plants. Of course, catalyst development work has to be done in order 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 during more than a day and impurities in the crude glycerol do not cause large problems with catalyst stability.

We consider that our results therefore pave the way for a new catalytic route from aqueous glycerol to methanol to be used to recycle the 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 does not require high pressure or hydrogen.

Methods

The MgO (**A**) catalyst was prepared by calcining high purity hydroxide (99% Sigma Aldrich) first at 723 K for 24 h. The resulting solid was then sieved between 250 and 425 µm followed by refluxing in water (15 mL g^{-1} for 3 h). The resulting slurry was dried at 383 K for 24 h then heated at 875 K under flowing N_2 (100 mL min^{-1}) for 3 h. A range of MgO catalysts (denoted (**B**) – (**D**)) were also prepared by varying the thermal treatment of the hydroxide precursor (see supplementary material). 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 1073 K under flowing N_2 for 3 h. Surface areas were determined according to the BET method.

Catalytic reactions were evaluated using a gas phase plug flow micro reactor (Figure S10 and S11 supplementary material). 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 a 8 mm 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, permitting typical gas hourly space velocities (GHSV) of 2000 to 24000 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 (PID) 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 subsequently collected. Crude glycerol was supplied by Biodiesel Amsterdam B. V. 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 capillary column (ZBWAX *plus*: i.d. 0.53 x 30 m). Gas samples were also collected and analyzed off-line by means of a Varian CP 3800 GC with a Porapack Q: 1/8”x 2 m column. Product selectivities, in mol. % were calculated from the moles of product recovered divided by the total moles of all products.

The liquid-phase products were analyzed 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% $Me_4Si/CDCl_3$ 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_2O were placed in an NMR tube along with the internal standard. A solvent suppression program was run in order to minimize the signal arising from the water. Chemical shifts were reported in parts per million relative to Me_4Si. 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 will readily form a stable derivative with the DNPH reagent. The derivative was eluted from the column with acetonitrile and analyzed by reverse phase chromatography using a PDA detector set at 360 nm. The presence of formaldehyde was confirmed via the comparison of retention times with that 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 only detected in trace ppm quantities.

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Author Contributions M.H.H. prepared and tested 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 authors contributed to the analysis of the data and the writing of the manuscript.

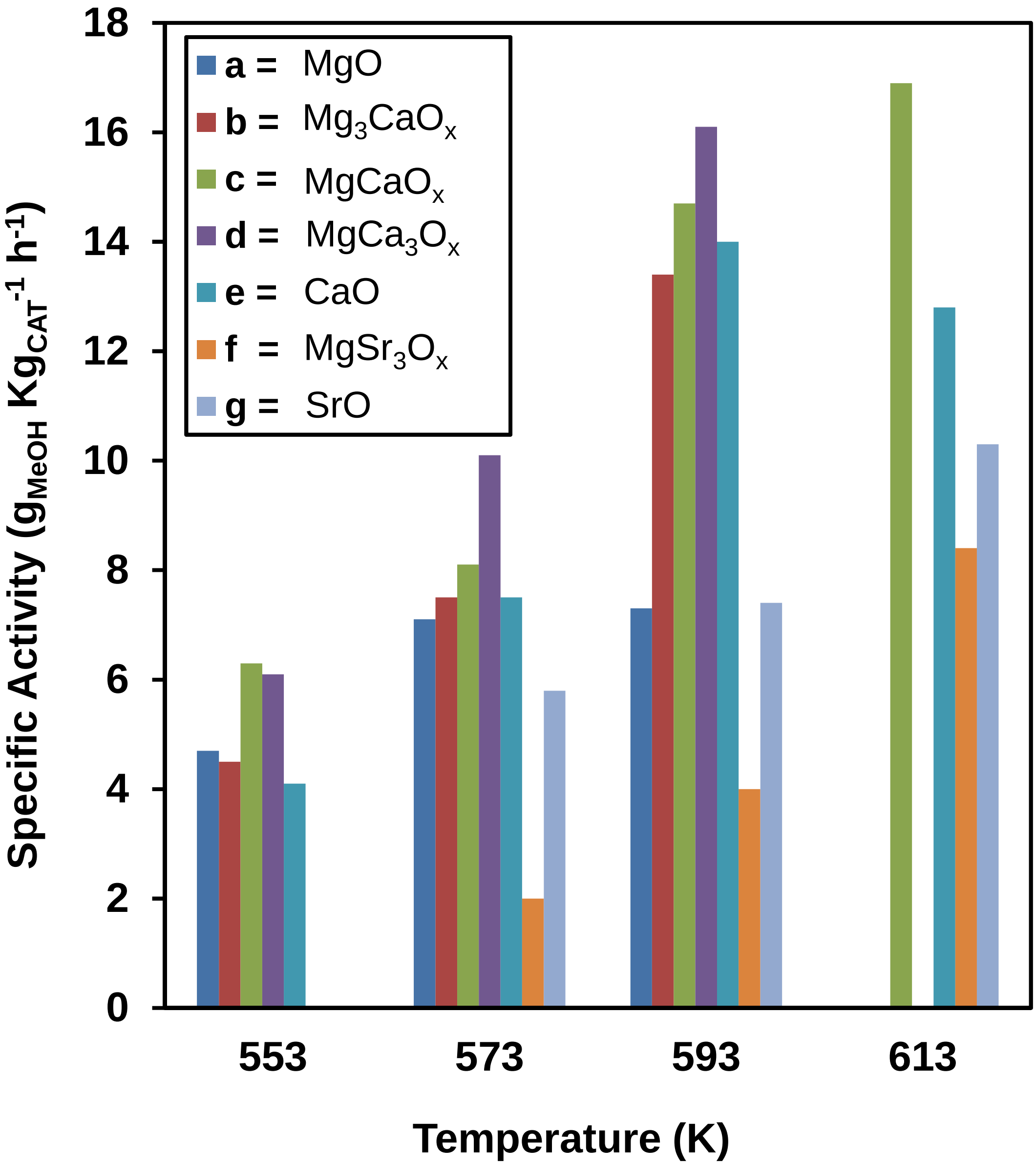


Figure 1 │ Catalytic activity of the metal oxide and mixed metal oxide materials. Specific activity defined as the grams of methanol produced per kilogram of catalyst per hour over (**a**) MgO (BET surface area:144 m^2g^{-1}), (**b**) Mg_3CaO_X (25 m^2g^{-1}), (**c**) $MgCaO_X$ (17 m^2g^{-1}), (**d**) $MgCa_3O_X$ (11 m^2g^{-1}), (**e**) CaO (13 m^2g^{-1}), (**f**) $MgSr_3O_X$ (3 m^2g^{-1}) and (**g**) SrO (3 m^2g^{-1}) is presented as a function of the reaction temperature. The activity of the catalysts generally increases with increasing temperature. The experiments were carried out in the 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}), 3 h. Full reaction data concerning conversion and selectivity are given in Supplementary Table S1

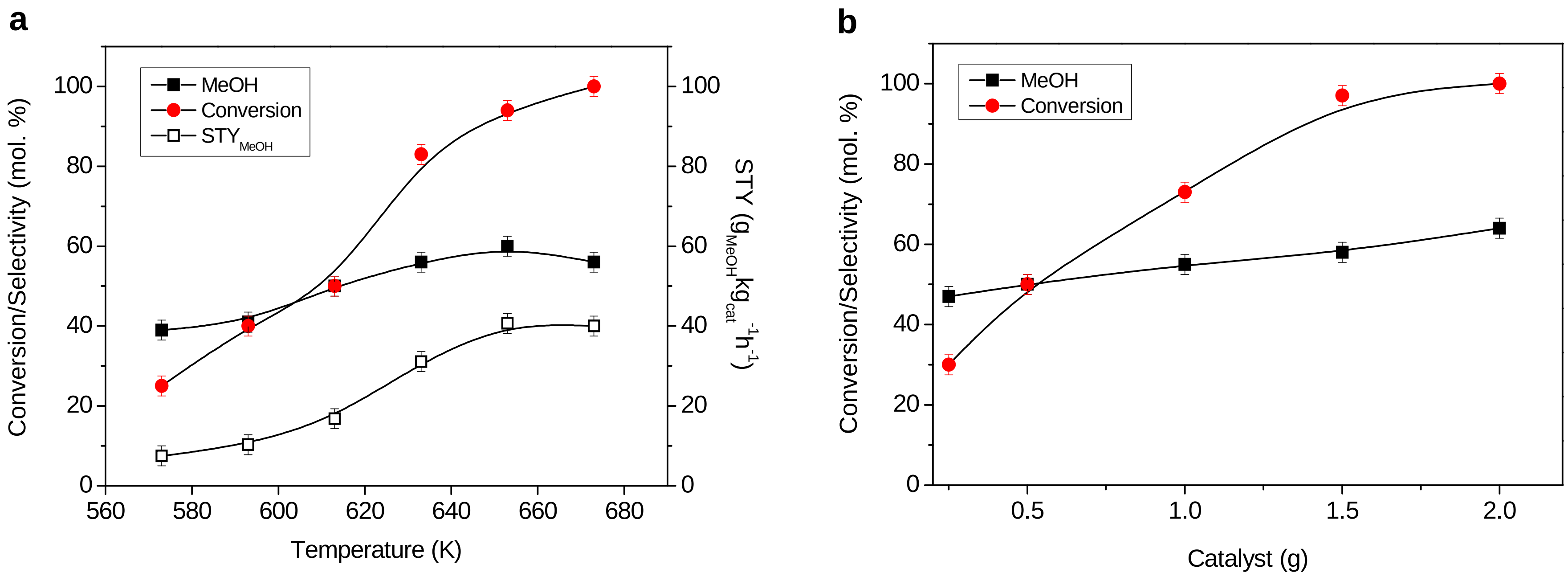


Figure 2 | Catalytic conversion of glycerol over cerium oxide and selectivity to methanol. a, Effect of temperature on the conversion (mol. %) of glycerol (10 wt. %) and methanol selectivity (mol. %) which indicates the space time yield of methanol reaches a plateau with increasing temperature. Experimental conditions: 0.5 g cat., 100 mL min^{-1} inert carrier, 1 mL h^{-1} feed flow, products collected for 3h. **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 3h. Experimental error is ± 5 % as represented by error bars.

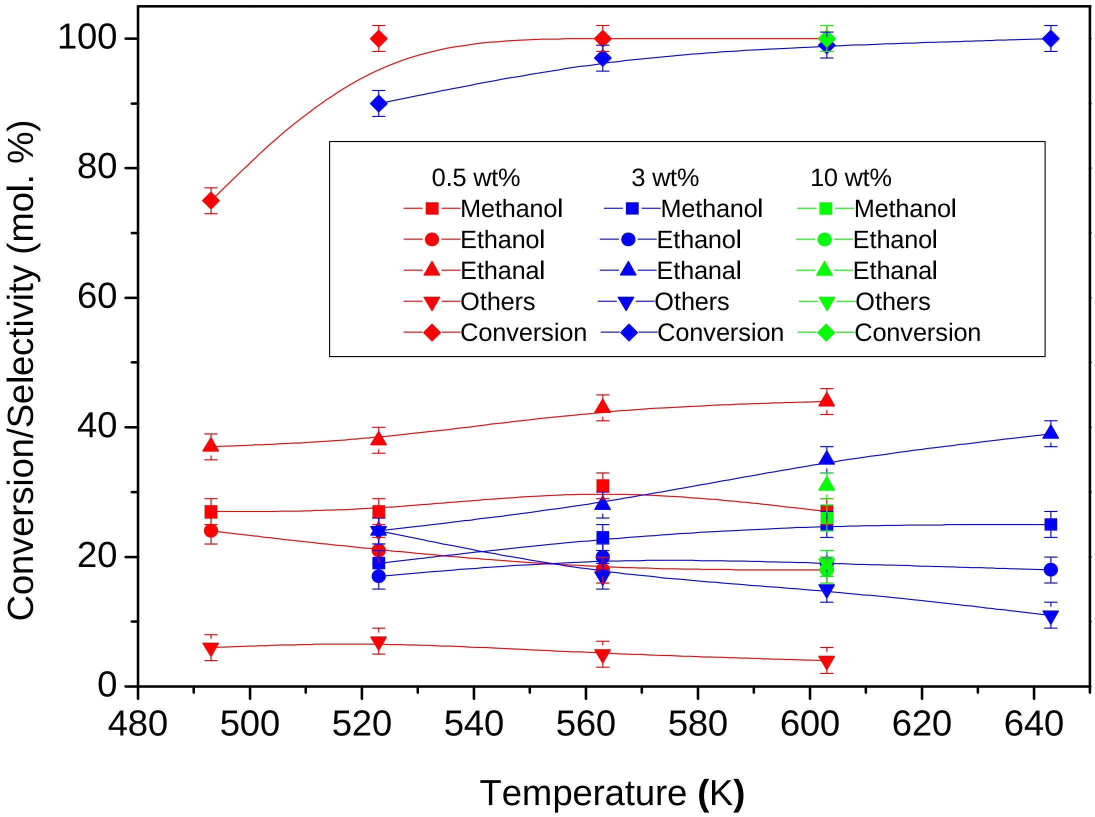
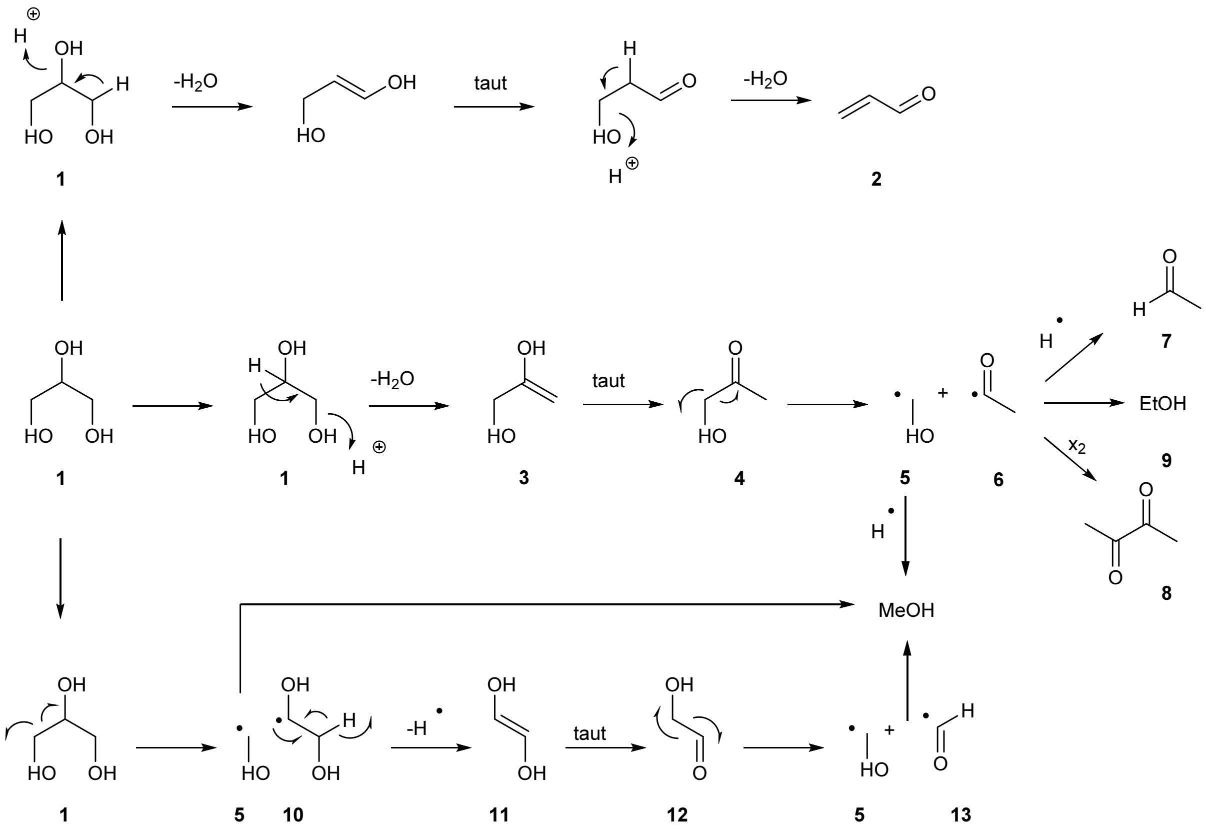


Figure 3 | The influence of reaction temperature on the conversion and product selectivities (mol %) over MgO (A) with different feed concentrations of 1,3-propanediol. The formation of methanol requires a reactant with at least two hydroxyl groups as no products were detected with 1- or 2-propanol.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



[taut = enol-keto tautomerism]

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

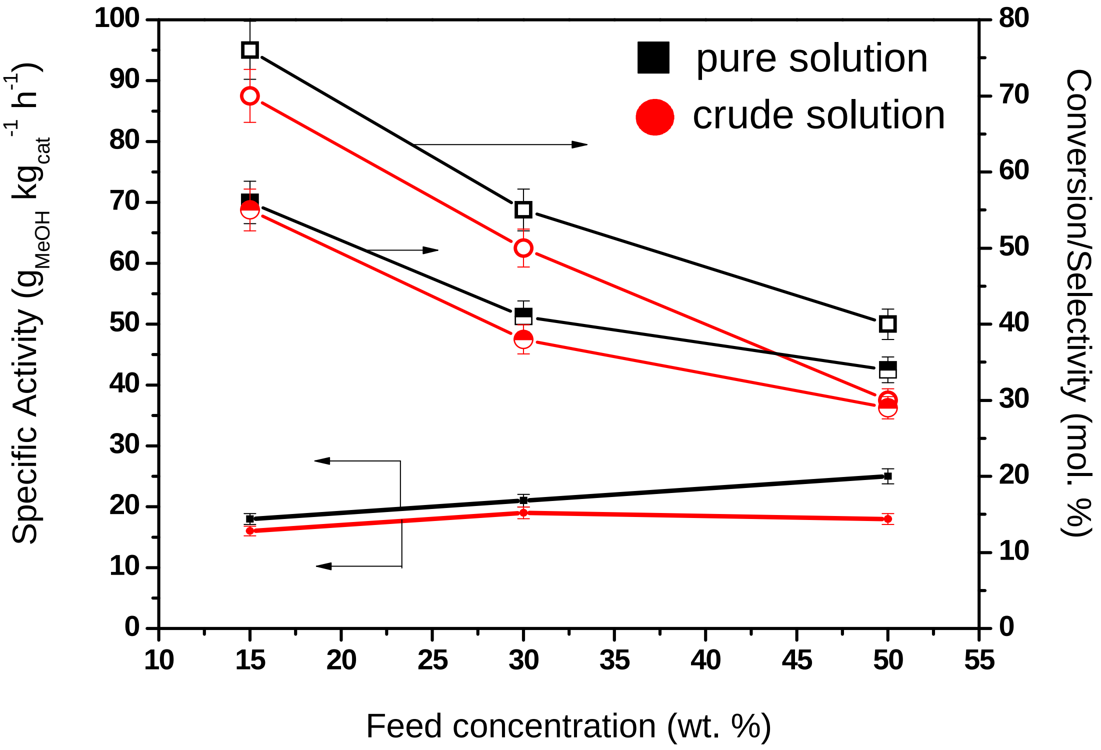


Figure 5 │ Catalytic activity of CeO_2 as an effect of increasing the glycerol feed concentration for both pure and crude glycerol. Specific activity is defined as the grams of methanol produced per kilogram of catalyst per hour. The pure glycerol solutions were prepared by diluting glycerol (99.9%) with water, whereas, the crude glycerol solutions were prepared by diluting crude glycerol (*ca*. 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 3 h conversion is lower than with the corresponding pure solutions. Glycerol conversion 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, 3 h duration at 613 K. Experimental error is ± 5 % as represented by error bars.