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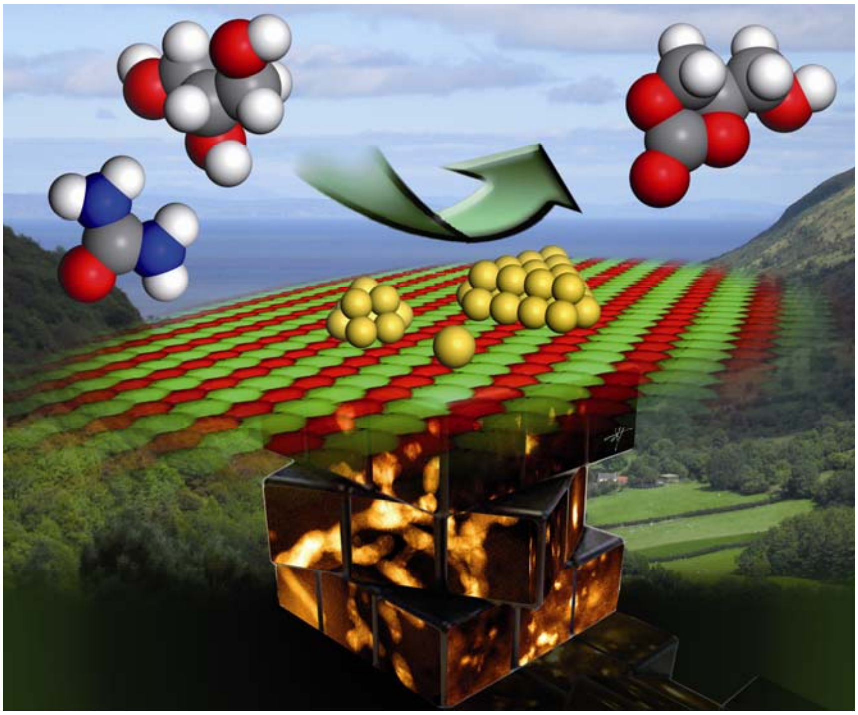

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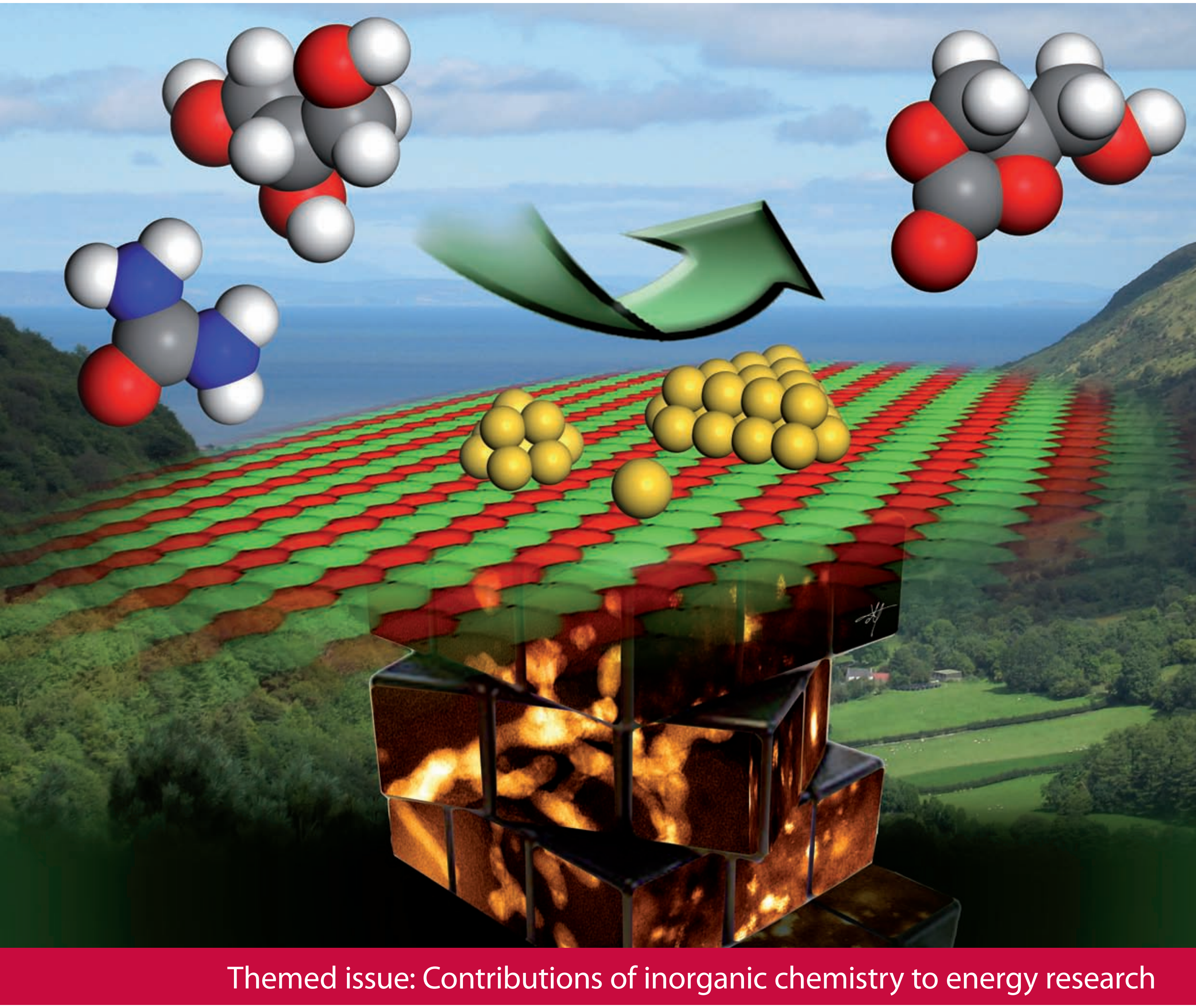

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PAPER

Synthesis of glycerol carbonate from glycerol and urea with gold-based catalysts†

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The reaction of glycerol with urea to form glycerol carbonate is mostly reported in the patent literature and to date there have been very few fundamental studies of the reaction mechanism. Furthermore, most previous studies have involved homogeneous catalysts whereas the identification of heterogeneous catalysts for this reaction would be highly beneficial. This is a very attractive reaction that utilises two inexpensive and readily available raw materials in a chemical cycle that overall, results in the chemical fixation of CO_2. This reaction also provides a route to up-grade waste glycerol produced in large quantities during the production of biodiesel. Previous reports are largely based on the utilisation of high concentrations of metal sulfates or oxides, which suffer from low intrinsic activity and selectivity. We have identified heterogeneous catalysts based on gallium, zinc, and gold supported on a range of oxides and the zeolite ZSM-5, which facilitate this reaction. The addition of each component to ZSM-5 leads to an increase in the reaction yield towards glycerol carbonate, but supported gold catalysts display the highest activity. For gold-based catalysts, MgO is the support of choice. Catalysts have been characterised by XRD, TEM, STEM and XPS, and the reaction has been studied with time-on-line analysis of products *via* a combination of FT-IR spectroscopy, HPLC, ^{13}C NMR and GC-MS analysis to evaluate the reaction pathway. Our proposed mechanism suggests that glycerol carbonate forms *via* the cyclization of a 2,3-dihydroxypropyl carbamate and that a subsequent reaction of glycerol carbonate with urea yields the carbamate of glycerol carbonate. Stability and reactivity studies indicate that consecutive reactions of glycerol carbonate can limit the selectivity achieved and reaction conditions can be selected to avoid this. The effect of the catalyst in the proposed mechanism is discussed.

Introduction

The impact of CO_2 emissions and global warming is a problem of interest for the whole of society, and the utilisation of CO_2 as chemical feedstock arises as a valuable alternative to storage methods aimed at mitigating CO_2 emissions. From a chemical perspective, CO_2 utilisation is an elegant and sustainable way to face the challenge of reducing the effect of CO_2 emissions and as a consequence, it is a matter of major interest for the whole scientific community and the inorganic chemistry community in particular.[1] Advances in CO_2 capture and utilisation have been reviewed in the recent literature intensively.[1,2] On the other hand, the utilisation of biomass and biodiesels in particular is now well established as a green alternative to reduce carbon emissions. One major drawback in the biodiesel industry is the by-production of large amounts of undesired glycerol during the transesterification process[3] which makes for a large surplus in the current glycerol market. Since the production of biofuels from biomass is increasing, the surplus production of glycerol is expected to continue for years to come. The utilisation of glycerol as a platform chemical represents an opportunity to obtain value added products from a highly functionalised and cheap raw material, and much research has recently been dedicated at finding new chemical pathways for the transformation of glycerol to value added products.[3–5] In particular, selective oxidation,[4,6–8] reduction to 1,3-propanediol[9] and etherification for its use as an additive for fuels have been the subject of much research.

Research in the synthesis of glycerol carbonate has only emerged in the last few years, and this is surprising since glycerol carbonate has excellent properties such as low toxicity, biodegradability and a high boiling point which make it a very attractive chemical for a variety of applications. Glycerol carbonate has found application as a high boiling polar solvent,[10] an intermediate

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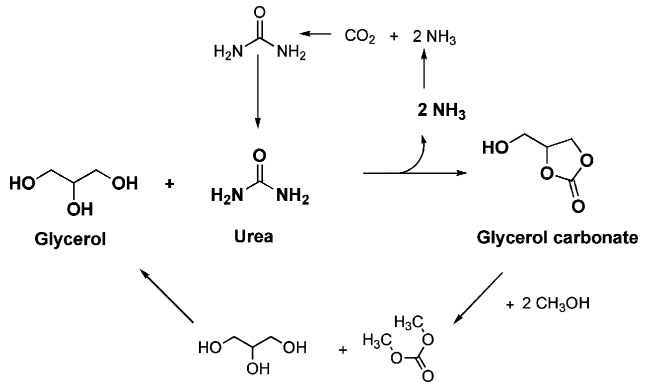
in organic synthesis[11] and in the synthesis of polycarbonates,[12,13] polyurethanes,[14] and surfactants. The traditional routes for synthesis of glycerol carbonate are typical of other low molecular weight organic carbonates. The reaction of glycerol with phosgene suffers from the drawbacks of using a dangerous and environmentally unfriendly reactant. The transesterification of glycerol can also be readily performed with dimethyl carbonate,[15] ethylene carbonate,[16,17] or propylene carbonate.[18] However, the carbonates utilised during the transesterification are typically generated *via* phosgene utilisation or energy intensive routes employing epoxides. While there are some reports addressing the direct carbonylation of glycerol with carbon dioxide with tin complexes, there are serious limitations for the applicability of such processes, particularly the unfavorable thermodynamic equilibrium and low yields.[19,20] The direct reaction of glycerol with supercritical CO_2 was also attempted using zeolites as catalysts,[21] however there is no evidence that a direct CO_2 insertion occurred as glycerol carbonate was only produced when another organic carbonate was added as a reactant. The above observations lead us to utilising urea as an alternative source for carbonylation. It can be argued that urea represents an activated form of CO_2. The reaction between CO_2 and ammonia producing urea is the most important process involving the chemical utilisation of CO_2 and about 10^8 tons of urea are produced per year worldwide. The industrial process utilises the Bosch–Meiser urea process, developed in 1922.[22] Overall, the reaction utilises two readily available and cheap reactants in a simple process that operates without a solvent, with high selectivity and yields under very mild conditions (Scheme 1). Until recently, most of the research was reported in the patent literature,[23–27] and while the reaction can proceed in the absence of a catalyst, several catalysts have been found to improve its rate. Homogeneous catalysis has been described with inorganic salts such as $ZnSO_4$,[26,28] and $MgSO_4$,[24,29] and more recently some heterogeneous systems based on oxides have been described.[17,30,31] To the best of our knowledge, no reports have been published using supported nanoparticles.



Scheme 1 Reaction setwork for glycerol carbonate synthesis using urea as CO_2 donor.

There are still many issues arising from these reports which highlight the need for developing new catalytic materials. Firstly, the reaction yield has only increased two fold from that of the uncatalysed reaction. Also the catalysed and uncatalysed reactions operate at the same temperature; clearly, reducing the reaction temperature could have important benefits considering the reactivity and stability of the products and, this should be a target for catalysis research. Secondly, there has only been limited research addressing the complete identification of reaction by-products, time on line activity studies and the role of the catalyst. Problems arising in the separation of the catalyst from the reaction mixture *via* the dissolution of the catalyst or formation of micropowders are important drawbacks. There is therefore a need for developing new heterogeneous catalysts which are highly active, fully heterogeneous, recoverable, stable and selective as well for a better understanding of the reaction mechanism.

Gold has attracted a huge amount of interest due to its activity as both a homogeneous and heterogeneous catalysis.[33] In particular, gold has been shown to selectively oxidise glycerol to glyceric acid in aqueous solution,[34] but also that it is a good catalyst for solvent-free selective oxidation of alcohols.[35] When gold is suitably supported on an appropriate oxide, it can also behave as a Lewis acid catalyst and these observations lead us to consider gold for the glycerolysis of urea. In this paper our initial results for this catalysed reaction are described. We have discovered that a number of heterogeneous catalysts are both very active and reusable, and in particular that gold can promote the formation of glycerol carbonate in the reaction of glycerol with urea.[32]

Experimental

Materials

The metal sulfate salts utilised in this work were tested as received from Sigma-Aldrich. Their purities are as follows: $ZnSO_4 \cdot H_2O$ 99.9+% trace metal basis, $MgSO_4$ 99.99+% trace metal basis and $VOSO_4 \cdot 3H_2O$ 99.99+% trace metal basis. $HAuCl_4 \cdot 3H_2O$, $PdCl_2$, (99.99% purity) and activated carbon (G60) were supplied by Johnson Matthey. Titania (P25) and SiO_2 were supplied by Degussa, zinc oxide (ZnO), magnesium oxide (MgO) and niobium oxide (Nb_2O_5) were supplied by Aldrich. ZSM-5 with a SiO_2/Al_2O_3 molar ratio of 30 was supplied by Zeolyst™ and used in its ammonium form in the synthesis of catalysts. The following metal salts were used: gallium(III) nitrate hydrate ($Ga(NO_3)_3 \cdot H_2O$) and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_20$) were obtained from Sigma-Aldrich.

Catalyst synthesis

Synthesis of catalysts by the impregnation method (I). Supported gold catalysts (2.5 wt% Au) were prepared by wet impregnation as follows. An aqueous solution of $HAuCl_4 \cdot 3H_2O$ (5.1 mL, 5 g dissolved in 250 mL) was added dropwise with stirring to the support (1.95 g). The resulting material was dried (110 °C, 16 h) and calcined (400 °C, 3 h, static air). Monometallic 1 wt.% Au/ZSM-5 catalysts were prepared following the same procedure using ZSM-5 (30) from Zeolyst in its ammonium form. Powder X-ray diffraction displayed the reflections due to gold metal on the various oxides utilised (Fig. S1 in ESI†).

Synthesis of catalysts by the deposition precipitation method (DP) (ref. 36). For the preparation of gold catalysts, an aqueous solution of $HAuCl_4 \cdot 3H_2O$ (3 mL, 2 g dissolved in 100 mL water) was added to distilled water (400 mL) containing a zeolite support (ZSM-5, 2.97 g) and urea (10 g). Upon pH stabilisation, the suspension was heated to 85 °C for 3 h in order to raise the resultant pH to 6.8–7.2. The suspension was subsequently filtered hot and washed with distilled water. The paste was dried overnight at 110 °C 16 h. The resulting material was dried (110 °C, 16 h) and calcined (400 °C, 3 h, static air). Ga-doped ZSM-5 was prepared in a similar manner, with the desired amount of gallium nitrate replacing aqueous $HAuCl_4{\cdot}3H_2O$. Zn-doped ZSM-5 was also prepared in accordance to the procedure described above, with the exception that urea was substituted for a 0.1 M aqueous ammonia solution, and the desired amount of zinc nitrate replaced aqueous $HAuCl_4{\cdot}3H_2O$.

Preparation of vanadium phosphate catalyst (ref. 37). V_2O_5 (11.8 g, Strem) was refluxed with H_3PO_4 (16.49 g, 85 wt.%, Aldrich) in isobutanol (250 mL) for 16 h. The light blue solid was recovered by filtration, washed with isobutanol (200 mL) and ethanol (150 mL, 100%), refluxed in water (9 mL H_2O (g solid)$^{-1}$) for 2 h, filtered and dried in air (110 °C, 16 h). Finally, the sample was calcined at 750 °C under a flow of nitrogen for 24 h in order to obtain the active $(VO)_2P_2O_7$ phase.

Reference gold catalysts. The two standard gold catalysts were obtained from the World Gold Council (4.5 wt.% Au/Fe_2O_3 (Lot No. 02-04) and 1 wt.% Au/TiO_2).[8,38]

Catalyst characterisation

Powder X-ray diffraction (XRPD) was performed using a PANalytical X'PertPRO X-ray diffractometer, with a Cu-Kα radiation source (40 kV and 40 mA). The diffraction patterns obtained were baseline corrected. Samples for examination by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were prepared by dispersing the catalyst powder in high purity ethanol, then allowing a drop of the suspension to evaporate on a holey carbon film supported by a 300 mesh copper TEM grid. Samples were then subjected to bright field imaging experiments using a JEOL 2000FX TEM operating at 200 kV. Phase contrast lattice imaging and high-angle annular dark field (HAADF) imaging experiments carried out using a 200 kV JEOL 2200FS transmission electron microscope equipped with a CEOS aberration corrector. X-Ray photoelectron spectra were recorded on a Kratos Axis Ultra DLD spectrometer employing a monochromatic AlK_α X-ray source (75–150 W) and analyser pass energies of 160 eV (for survey scans) or 40 eV (for detailed scans). Samples were mounted using double-sided adhesive tape and binding energies referenced to the C(1 s) binding energy of adventitious carbon contamination which was taken to be 284.7 eV.

Catalyst testing

The synthesis of glycerol carbonate was performed as follows. Glycerol (typically 13.8 g, 0.15 moles) was added to a round bottom flask (100 mL) and dried at the desired reaction temperature (150 °C) under a flow of dry nitrogen for 20 min. The desired amount of urea (typically 13.5 g, 0.225 moles (molar ratio glycerol : urea 1 : 1.5)) was then added, and once solubilised, the desired catalyst (250 mg) was added. Dry nitrogen was passed through the reaction mixture in order to remove any NH_3 formed. The reaction was sampled periodically, and the samples obtained were diluted to 0.0375 M for analysis by HPLC.

The stability of glycerol carbonate was determined as follows; glycerol carbonate (13.8 g, 0.117 moles) was placed in a round bottom flask (100 mL) and heated at 150 °C for 24 h under a flow of dry nitrogen. Samples were subsequently analysed by HPLC (previously described). The reaction between glycerol carbonate and urea was performed as described above, except that glycerol was substituted by glycerol carbonate (13.8 g, 0.117 moles).

Analysis of products

^1H and ^{13}C NMR spectra were recorded at room temperature on a Bruker DPX 500 (^{13}C 125.77 MHz) for dilute solutions. Proton chemical shifts are reported in parts per million relative to Me_4Si. ^{13}C Spectra were referenced to the ^{13}C resonance of the NMR solvent (CD_3OD $\delta = 48.97$). Mass spectrometric analyses were carried out on a Waters LCT Premier XE operating in the APCI (+ve) mode. The reaction mixture was infused into the MS source *via* a syringe pump at a rate of 10 μl min^{-1}. FT-IR spectroscopy was performed by placing the neat reaction mixture between two NaCl plates, with the spectra recorded on a Jasco FT-IR660 Plus over a range of 4000–400 cm^{-1} at a resolution of 2 cm^{-1}. Quantification of the reaction products was carried out on a Varian 920LC HPLC using ultraviolet and refractive index detectors. The eluent was an aqueous solution of H_3PO_4 (0.01 M) and the flow was 0.45 ml min^{-1}. Samples of the reaction mixture were diluted using the eluent to a concentration of 0.0375 M concentration. Reactants and products were separated using a Metacarb 67H column and the products identified by comparison with authentic samples. For quantitative analysis, an external standard method was used.

Results and discussion

Microscopy of the zeolite-supported catalysts

Fig. 1(a) is a typical bright field TEM micrograph of the 3.5 wt.% Ga/ZSM-5 catalyst, prepared by deposition precipitation in urea. This image shows Ga-oxide particles about 3–5 nm in size uniformly distributed on the zeolite support. Fig. 1(b) corresponds to the 3.5 wt.% Zn/ZSM-5 material, prepared by deposition precipitation in ammonia. Large agglomerates of bulk ZnO particles as well as a more dilute distribution of smaller (~5 nm) ZnO nanoparticles scattered over the ZSM-5 support are apparent.

The Au/ZSM-5 samples were also examined by TEM in order to compare the morphologies of the samples made by wet impregnation and deposition precipitation with urea. It was found that these different preparation methods produced very different results in terms of Au dispersion on the zeolite support (see Fig. 2). In the deposition precipitation (urea) sample, the Au formed characteristic sintered 'chain-like' structures about 5–8 nm in width (see Fig. 2(a)). In contrast, discrete Au particles around 2–5 nm in diameter were the predominant Au morphology present in the sample prepared by impregnation (see Fig. 2(b)).

Microscopy of the magnesia-supported Au catalysts

Fig. 3(a) shows a representative bright field TEM image of the fresh 2.5 wt% Au/MgO sample prepared by impregnation which was calcined at 400 °C. Discrete Au particles ranging between about

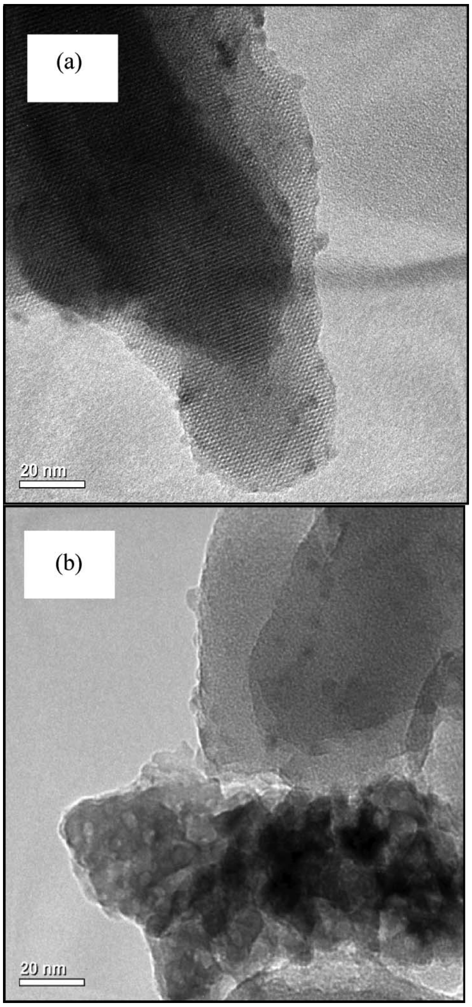


Fig. 1 Bright field micrographs of (a) 3.5 wt.% Ga/ZSM-5 and (b) 3.5 wt.% Zn/ZSM-5, both prepared by deposition precipitation.

5 and 20 nm in size are clearly visible against the flake-like MgO support material. HAADF imaging shows that discrete Au atoms (Fig. 3(b)) and occasional 1–2 nm raft-like Au clusters (Fig. 3(c)) also co-exist on the MgO support. We were unable to acquire the corresponding electron HAADF images from the used 2.5 wt% Au/MgO sample material as the support had become extremely beam sensitive and drilled rapidly under the electron probe. In order to understand this effect, XRD of the 2.5%Au/MgO catalyst was performed before and after use (Fig. S2 in ESI†). The XRD revealed the appearance of the reflections typical of gold nanoparticles in the fresh sample, which are attributable to gold in the metallic state ($2\theta = 38.1°$, 44.2° and 64.6°) and that no significant changes in the crystalline structure of the magnesium oxide resulted from the synthesis. However, after 9 uses, the sample displays only the gold reflections, indicating that the support has changed during reaction and lost crystallinity, however, that the gold nanoparticles are still supported.

Catalytic activity

Activity of homogeneous catalysts for glycerol carbonate formation. Catalytic testing was performed under previously reported reaction conditions but, in order to remove the ammonia formed during reaction, nitrogen was bubbled through the reaction mixture instead of applying vacuum. Homogeneous metal sulfates ($ZnSO_4$ in particular) were shown to be particularly active for the reaction, and this was corroborated in the experiments plotted in Fig. 4. In addition to reproducing the activity of $ZnSO_4$ and $MgSO_4$ reported in the literature,[23,28] it was also found that $VOSO_4$ was an active catalyst for this reaction. It is notable that all the metal sulfate catalysts studied resulted in an increase in glycerol carbonate yield, this suggests that the study of the role of cation and anion in these systems are worth of study in future work. It can be seen in Fig. 4 that while the yield of glycerol carbonate increases linearly for all the catalysts for the first 6 h of reaction, there is however, a significant contribution of the uncatalysed homogeneous reaction. In these experiments 8.6 wt% of catalyst was used with respect to glycerol, and this high percentage emphasises the poor activity of these catalysts. In order to develop precious metal supported catalysts and reduce the amount of wasted catalyst, later reactions were carried out with a decreased mass of catalyst (1.8 wt% with respect to glycerol).

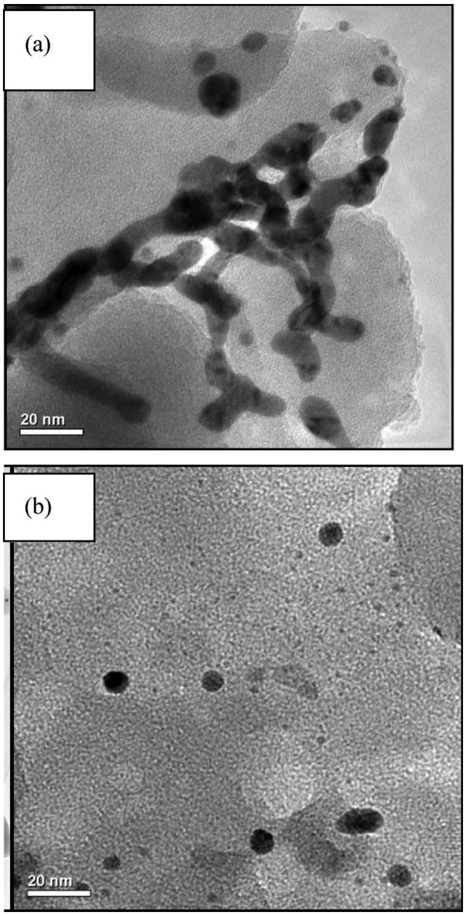


Fig. 2 Bright field micrographs of 1 wt.% Au/ZSM-5 catalysts prepared by (a) deposition-precipitation with urea and (b) and *via* wet impregnation.

Activity of a range of heterogeneous catalysts. A number of heterogeneous catalysts were screened (Fig. 5). The catalyst loading was lower than that previously utilised for $ZnSO_4$ and other recent publications,[17] and because of this, the relative ratio between activity for the catalysed and uncatalysed reaction decreased significantly when compared to the results shown

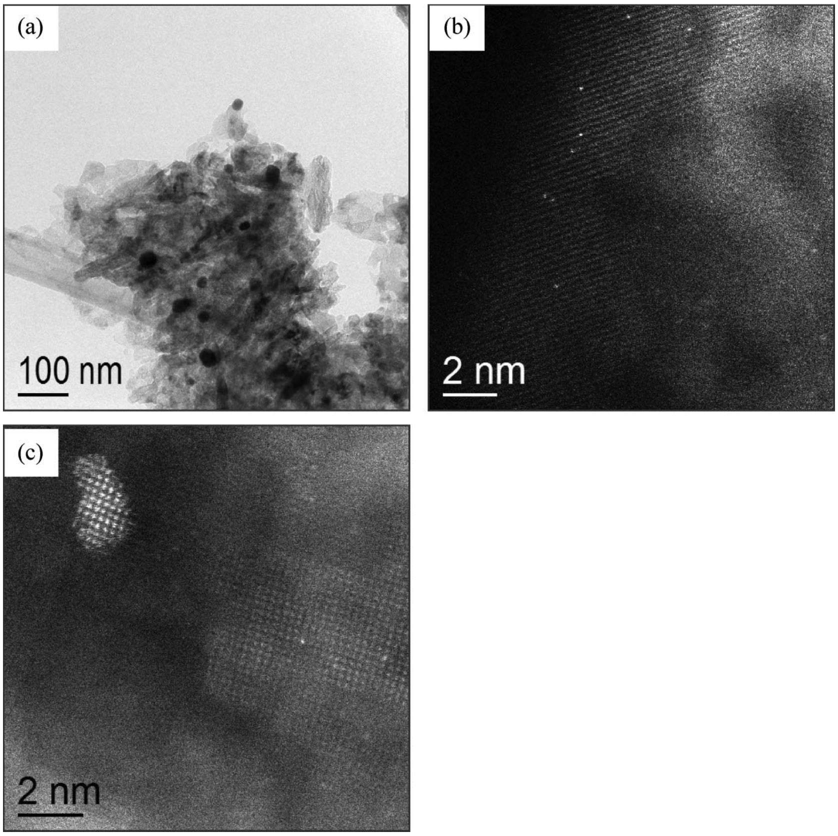


Fig. 3 Representative BF-TEM (a) and STEM-HAADF images (b,c) of sample MH-01: 2.5% Au/MgO (imp, cal 400 fresh).

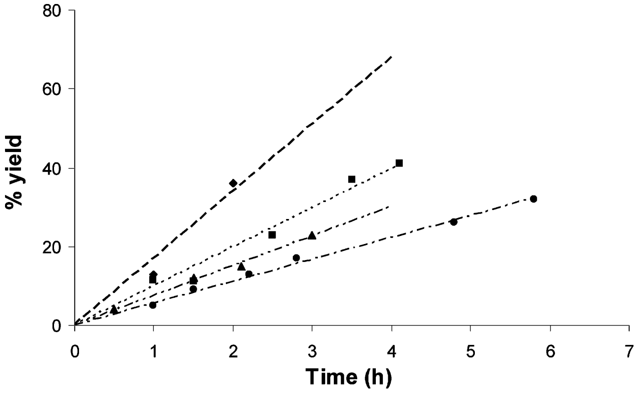


Fig. 4 Glycerol carbonate yield for a series of homogeneous metal sulfate catalysts. Conditions: catalyst: (4.74 g), reactants: glycerol/urea: 1 : 1 molar ratio, temperature: 150 °C, time: 6 h. Key: ◆ = $ZnSO_4$; ■ = $MgSO_4$; ▲ = $VOSO_4$; ● = No catalyst.

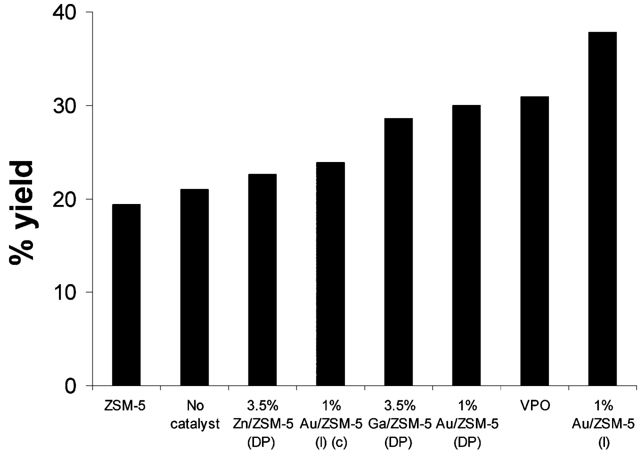


Fig. 5 Glycerol carbonate yield obtained with various zeolite supported Au, Ga and Zn catalysts prepared by deposition precipitation (DP) and impregnation (I). Typical catalyst pre-treatment conditions: 110 °C for 16 h, with the exception of 1 wt.% Au/ZSM-5 (I) (c) which was calcined at 400 °C in static air for 3 h. Reaction conditions: glycerol/urea molar ratio: 1 : 1, temperature: 150 °C, catalyst: 0.25 g, reaction time: 4 h.

in Fig. 4. In order to emulate the activity of $ZnSO_4$ with a heterogeneous catalyst, our first approach was to deposit Zn on zeolite ZSM-5 by deposition-precipitation, taking advantage of the high surface area of ZSM-5 as a support to disperse Zn. Firstly it became apparent that while ZSM-5 had some level of activity, it resulted in slightly lower glycerol carbonate yields with respect to the uncatalysed reaction. However, the deposition of Zn, Ga and Au onto ZSM-5 by deposition precipitation resulted in an enhancement in glycerol carbonate yield in all cases, with the order of promotion following the order: Au > Ga > Zn.

It is also clear that the preparation procedure used during the synthesis of the gold catalyst has an effect on the catalytic activity, as Au/ZSM-5 was shown to be more active when prepared by impregnation as opposed to deposition precipitation (Fig. 5). It has been described that the catalytic activity of homogeneous metal sulfates may be due to their Lewis acid character,[23,28] and our initial XPS results with the above series of heterogeneous

Au/ZSM-5 catalysts appears in agreement with this. In Fig. 6 the Au(4f) spectra from the Au/ZSM-5 catalysts prepared by impregnation (IMP) and deposition-precipitation (DP) before and after calcination at 400 °C are shown. The dried materials contain cationic gold species: the IMP sample comprises mainly Au^+ ions and the DP sample a mixture of Au^{3+} and Au^+ species. In contrast, both catalysts contain only Au^0 species after calcination at 400 °C. It is clear from Fig. 5 that the calcination of Au/ZSM-5 has a negative impact on the catalytic activity, and this may be due to the decrease in cationic gold in the catalyst. As well as the possible influence of cation distribution on activity, we must also consider the morphology of the gold deposited on to ZSM-5. It can be observed in Fig. 6, that while the impregnation of gold on to ZSM-5 results in the formation of discrete Au particles around 2–5 nm in diameter, deposition precipitation results in the formation of sintered 'chain-like' structure around 5–8 nm in width, but over 100 nm in length. While the deposition precipitation sample exhibits a 50% increase in glycerol carbonate yield over the uncatalysed reaction, its catalytic activity is significantly lower than that of the impregnated sample. The large chains of gold present on the catalyst surface would presumably result in increased metallic character and a potential decrease in catalytic activity *versus* the discrete nanoparticles present in the impregnated sample. As a consequence, later materials were prepared by the impregnation method.

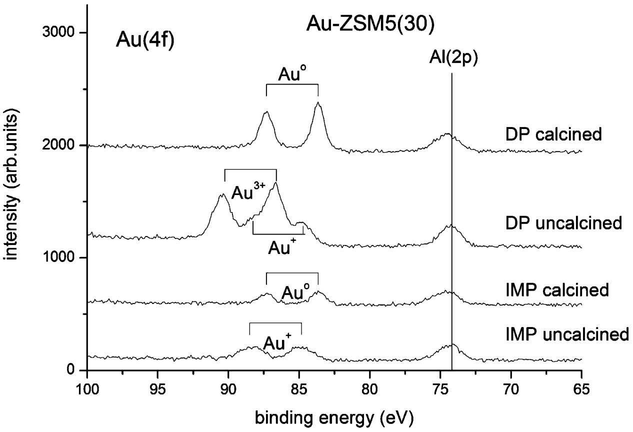


Fig. 6 Au(4f) spectra for a series of Au/ZSM-5 catalysts prepared by deposition precipitation (DP) and impregnation (IMP).

Due to the activity displayed by $VOSO_4$ in the homogeneous reaction (Fig. 4), the activity of a vanadium phosphorous oxide (VPO) catalyst was evaluated. VPO materials are known for providing Lewis acid and basic functionalities, and some recent reports have highlighted their activity for glycerol conversion reactions.[39,40] The catalyst was prepared by the organic route and treated at 750 °C under nitrogen to produce the $(VO)_2P_2O_7$ catalytic phase. The calcination process ensures that the vanadyl hemihydrate phase present in the precursor fully transforms to the vanadyl pyrophosphate, which is insoluble under reaction conditions. The results were surprisingly good as displayed in Fig. 5, improving the glycerol carbonate yield by some 50%, relative to the uncatalysed reaction. However, a gold catalyst supported on ZSM-5 displayed better glycerol carbonate yield and the performance of gold supported catalyst will be the main focus for the rest of this research paper.

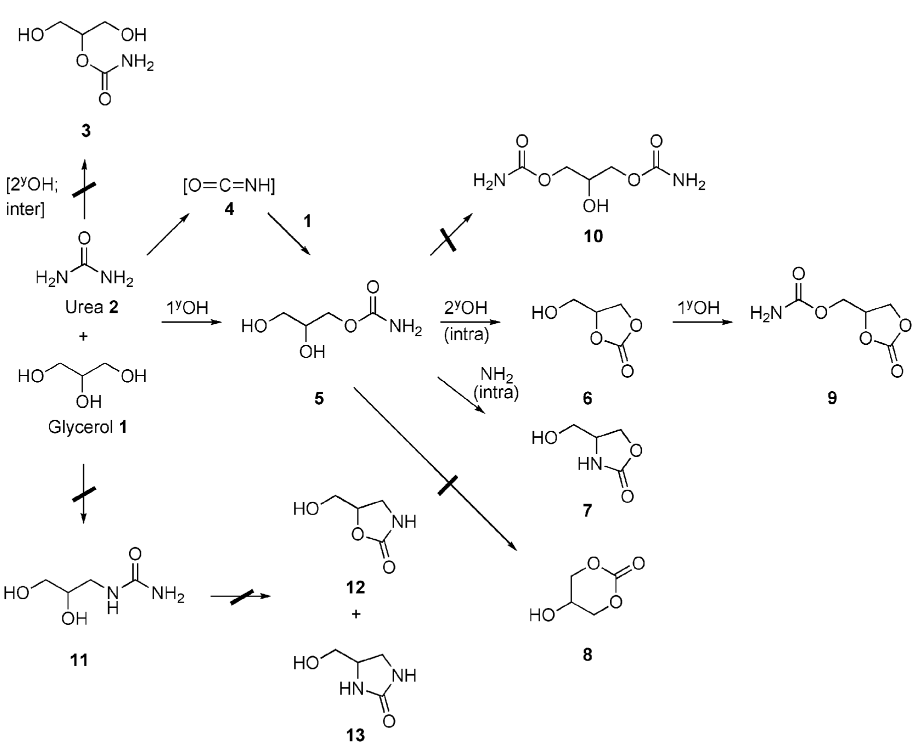
Table 1 Catalytic activity of gold catalysts supported on several supports[a]

Entry	Catalyst	Conv. (%)	Selectivity (%) Glycerol carbonate	**5**	**7**	**9**	Glycerol carbonate yield (%)
1	Blank	59	36	44	7	13	21
2	$ZnSO_4$	83	58	20	5	17	48
3	Au/TiO_2[b]	69	37	36	9	18	26
4	Au/Fe_2O_3[b]	80	48	26	9	17	39
5	2.5wt%Au/C	66	34	38	9	19	22
6	2.5wt%Au/SiO_2	73	39	33	6	22	23
7	2.5wt%Au/Nb_2O_5	66	32	37	10	21	21
8	2.5wt%Au/TiO_2	77	37	32	11	20	29
9	2.5wt%Au/ZnO	88	56	17	7	20	49
10	2.5wt%Au/MgO	81	68	16	4	12	56
11	2.5wt%Au/MgO After 10th use	80	69	17	4	10	55
12	MgO	69	37	37	10	16	26

[a] Reaction conditions: glycerol/urea molar ratio: 1 : 1.5, temperature: 150 °C, catalyst: 0.25 g, time: 4 h. Product (**5**) = 2,3-dihydroxylpropyl carbamate, product (**7**) = 4-(hydroxymethyl) oxazolidin-2-one, product (**9**) = (2-oxo-1,3-dioxolan-4-yl) methyl carbamate. [b] World Gold Council reference catalysts.

Activity of gold catalysts. In the following catalytic studies, full quantitative analysis of all reaction products was obtained, and therefore selectivities are now calculated in addition to glycerol carbonate yields. The possible reaction products have been drawn and numbered in Scheme 2. The reaction products detected were 2,3-dihydroxypropyl carbamate (**5**), glycerol carbonate (**6**), 4-(hydroxymethyl) oxazolidin-2-one (**7**) and (2-oxo-1,3-dioxolan-4-yl)methyl carbamate (**9**). The results obtained with a range of gold catalysts supported on oxides or carbon are displayed in Table 1.

To study the effect of the support on catalyst performance, six gold catalysts were prepared by impregnation of gold onto carbon, silica, niobium oxide, titania, magnesium oxide and zinc oxide with a 2.5 wt% loading. The catalytic activity of each catalyst after 4 h reaction is displayed in Table 1 in entries 5–10. For comparison, the catalytic activity of homogeneous $ZnSO_4$ (entry 2) tested under our standard reaction conditions, and the activity of two reference catalysts supplied by the World Gold Council (Au/TiO_2 and Au/Fe_2O_3; entries 3 and 4 respectively) are displayed. The authors have previously shown that the two gold reference materials are very active for oxidation and hydrogenation reactions[8,38] and it is evident that all the gold catalysts produced higher glycerol carbonate yields compared to the uncatalysed reaction (entry 1). This appears to be due to an increase in conversion but also to an increase in reaction selectivity toward glycerol carbonate, especially for the catalysts supported on magnesium oxide. The results indicate large differences in catalytic activity and the support seems to play a fundamental role. In particular, 2.5wt%Au/MgO gave the highest glycerol carbonate yield as it displayed over 80% conversion and selectivity to glycerol carbonate of almost 70% after 4 h. When compared to the activity of the support alone (entry 12), the presence of gold improves both glycerol conversion and glycerol carbonate selectivity. As a result, the catalytic performance and morphology of 2.5 wt% Au/MgO was studied further in detail. The re-usability of the catalyst (2.5 wt% Au/MgO calcined at 400 °C) was evaluated for a total of ten catalytic cycles. Entry 11 in Table 1 indicates that the catalyst retains both its high activity and selectivity to glycerol



Scheme 2 Possible reaction pathways for the reaction between glycerol and urea.

carbonate after the ten cycles (see Table S1 in ESI for full set of data†).

Despite the apparent simplicity of the reaction of glycerol with urea, this reaction can take a large number of possible pathways (Scheme 2). One might expect that at the given reaction conditions, many of the pathways displayed in Scheme 2 will be possible and this adds complexity of the reaction and mechanistic details. There have been a number of reports that describe the presence of several of the products displayed (Scheme 2), but these are not in full agreement. The presence of specific by-products is important to understand the effect of the catalyst in the reaction, and to elucidate some of the mechanisms occurring with or without catalyst. Hence, a set of time on line measurements was performed for 7 h using FT-IR, ^{13}C NMR, MS and HPLC to fully identify and quantify all reaction products.

The reaction profile (Fig. 7) indicates that after 2 h *ca.* 70% of glycerol has been converted and that conversion levels off. The reaction is carried out in pure glycerol and, as the reaction progresses, the concentration of glycerol decreases slowing the kinetics of the reaction (see Fig. S3 in ESI for molar composition of the reaction mixture†). The presence of large amounts of 2,3-dihydroxypropyl carbamate (**5**) in the initial stages of the reaction suggests that it is formed in the first step. While compounds **7** and **9** were also detected in small percentages, but the selectivity of glycerol to form these products drops immediately for compound **7** and after 2 h for compound **9**. On the other hand, selectivity to glycerol carbonate increases with conversion over the range of time studied.

FT-IR spectra of samples taken at 1 and 4 h are displayed in Fig. 8. The isocyanic acid (**4**) N=C=O stretching band at 2250 cm^{-1} is not present and we can therefore exclude the mechanism in which isocyanic acid (**4**) is produced as the primary product of the reaction. This is in agreement with observations by Aresta *et al.*[30] for their phosphated zirconia systems, who similarly claim that in the presence of their catalysts the reaction mechanism does not proceed *via* isocyanic acid as found for ZnSO$_4$, but *via* 2,3-dihydroxypropyl carbamate (**5**) instead. This is also important because the formation of isocyanic acid and its oligomers would represent the unselective use of urea. Fig. 8 also shows the bands corresponding to urea at 1620 cm^{-1} and 1670 cm^{-1} after 1 h reaction, and how they decrease in intensity with time on line. This is in agreement with the values of glycerol conversion calculated, indicating that conversion increases rapidly for the first hours of the reaction and level off after 5–7 h, when urea and glycerol

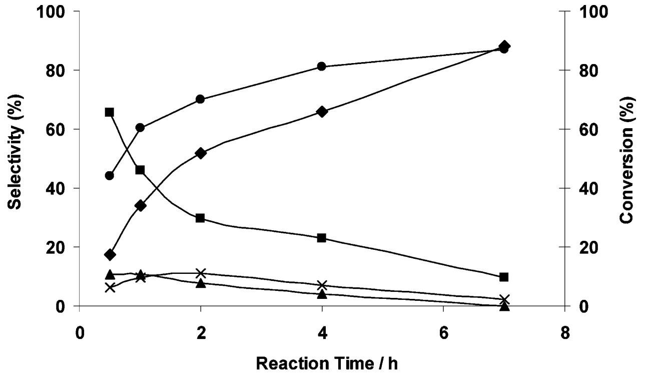


Fig. 7 Time online analysis for 2.5 wt.% Au/MgO (I) and calcined at 400 °C in the reaction of glycerol with urea. Reaction conditions: glycerol/urea molar ratio: 1 : 1.5, temperature: 150 °C, catalyst: 0.25 g, reaction time: 7 h. Key: ◆ selectivity to glycerol carbonate (6), ■ selectivity to 2,3-dihydroxyproyl carbamate (5), ▲ selectivity to 4-(hydroxymethyl) oxazolidin-2-one (7), × selectivity to (2-oxo-1,3-dioxolan-4-yl) methyl carbamate (9) and, ● glycerol conversion.

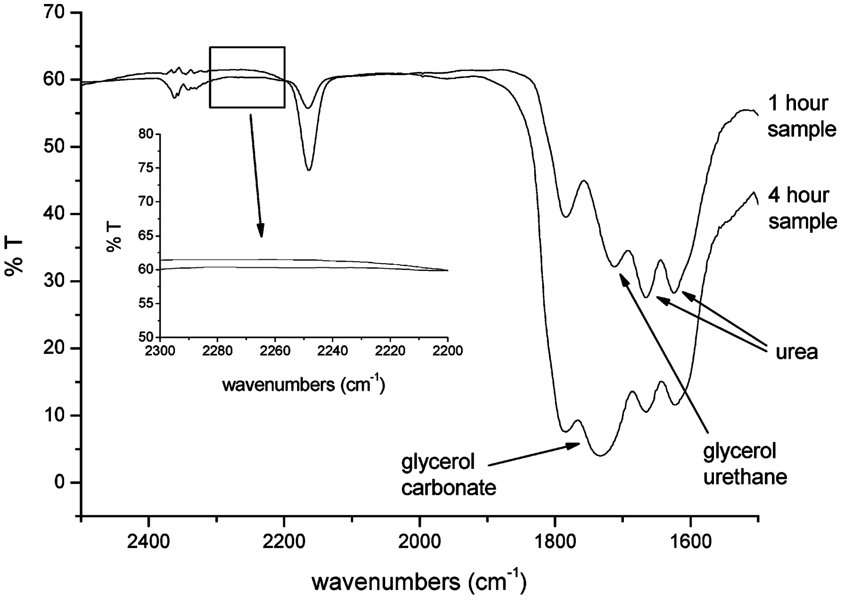


Fig. 8 FT-IR spectra of reaction samples taken after 1 and 4 h for the reaction of glycerol with urea at 150 °C in the presence of 2.5 wt.% Au/MgO (I). The region between 2300–2200 cm^{-1} is expanded and illustrated within the figure to evidence the absence of isocyanic acid.

concentrations become significantly lower. The band corresponding to 2,3-dihydroxypropyl carbamate (**5**) at 1710 cm^{-1} is also evident at early TOL but diminishes with time as the intermediate is transformed in to glycerol carbonate. The spectroscopic analysis also shows that glycerol carbonate concentration increases with time as expected. All the features observed in the IR spectra have been assigned with the help of the literature[30] with the exception of an unknown band at *ca.* 1780 cm^{-1}. It must be noted that Aresta *et al.*[30] also reported an unknown product in their catalytic studies, which was present in their ^{13}C NMR spectra, but they did not fully identified. We propose that this peak is due to the formation of (2-oxo-1,3,-dioxolan-4-yl)methyl carbamate, this is because glycerol carbonate has a primary hydroxyl group available to react with urea to form the **9** (Fig. 9). This is following the same mechanism that favours the formation of **5** and it is therefore not surprising that this reaction occurs. The presence of compound **9** was later confirmed by MS analysis, which was also definitive in the assignments of the other reaction products. MS indicated the presence of the following masses in the reaction mixture; 135, 118, 117 and 161, which are in agreement of the

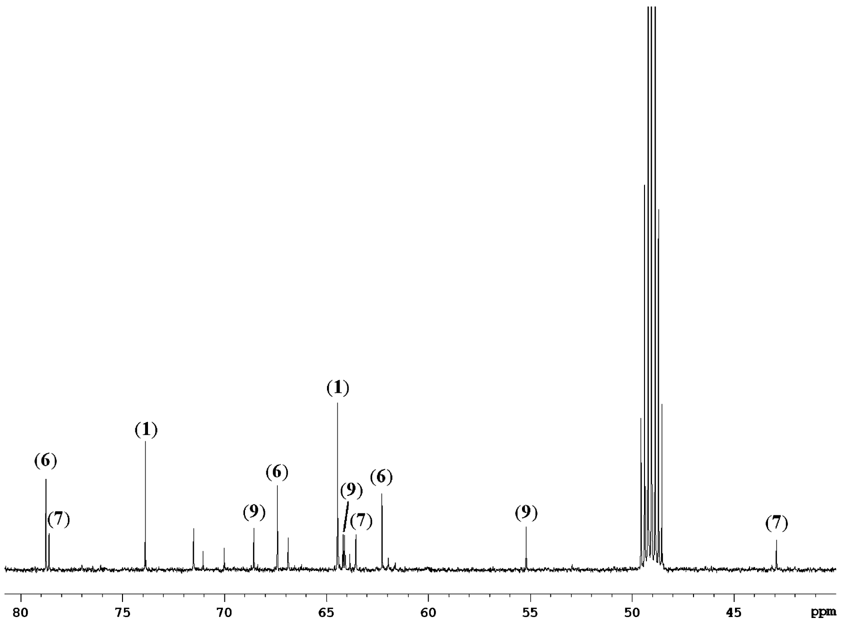


Fig. 9 ^{13}C NMR spectroscopy of the reaction mixture obtained after a 4 h reaction catalysed by 2.5 wt.% Au/MgO (I) and calcined at 400 °C. Key: (1) = glycerol; (6) = glycerol carbonate; (7) = 4-(hydroxymethyl)oxazolidin-2-one; (9) = (2-oxo-1,3,-dioxolan-4-yl)methyl carbamate. Small unlabelled peaks belong to an impurity which concentration did not change during reaction.

reaction products **5**, **6**, **7** and **9** respectively. From the above, it is evident that glycerol and urea readily react to produce 2,3-dihydroxypropyl carbamate (**5**) as the only initial product, which can subsequently undergo an intramolecular cyclisation, either eliminating ammonia to yield glycerol carbonate (**6**) or eliminating water resulting in the formation of 4-(hydroxymethyl)oxazolidin-2-one (**7**), this compound also having been identified by other researchers at concentration levels of *ca.* 2%.[17] It must be noted that mass 117 also corresponds to the isomer compound **12**, but complementary NMR and MS studies confirm that none of compound **11** was formed and therefore we can completely exclude the reaction pathway whereby urea reacts with the primary hydroxyl of glycerol eliminating water and creating a C–N bond. Glycerol carbonate is therefore formed preferentially, and it then it can subsequently react with urea to yield (2-oxo-1,3-dioxolan-4-yl)methyl carbamate (**9**), which was also been detected by Climent *et al.*[17] at similar concentration levels. It must be noted that Climent *et al.*[17] have also evaluated magnesium and zinc oxides and improved the yield of glycerol carbonate up to 72% by using a Zn–Al hydrotalcite catalyst using more favourable reaction conditions (glycerol/urea molar ratio = 1, reduced pressure of 30 Torr, 145 °C, 5 wt% catalyst at 5 h reaction time).

In order to corroborate the mechanism of formation of compound **9**, glycerol carbonate was heated at 150 °C under a flow of N_2 and in the absence of urea. Glycerol carbonate was quite stable and only *ca.* 5% of the compound was lost in 24 h. However, when urea was added and the same experiment was performed high conversions of glycerol carbonate were observed (see Fig. S4 in ESI†). Under these conditions glycerol carbonate readily reacts with urea to yield (2-oxo-1,3-dioxolan-4-yl)methyl carbamate (**9**) with almost 50% conversion after only 30 min. A total of 70% of glycerol carbonate had been converted after 4 h and the major product detected by MS was still compound (**9**). Of course, this fast reaction does not normally occur to great extent during the synthesis of glycerol carbonate because it must compete with the faster reaction of glycerol with urea and urea concentration decreases significantly by the time that high concentrations of glycerol carbonate are present in the reaction mixture. This is in agreement with the reaction mechanism proposed and emphasises the importance of controlling the glycerol/glycerol carbonate ratios during reaction to avoid consecutive undesired reactions.

The observations above suggest that variations in the ratio between glycerol and urea will have important effects on the product distribution. The effect of the glycerol/urea ratio in the uncatalysed reaction is displayed in Table 2. In these experiments, the reaction parameters were kept constant but the initial amount of urea was varied. Increasing the glycerol/urea molar ratio has the obvious consequence of reducing glycerol conversion, as not enough urea is present and becomes the limiting reactant. So that with a glycerol to urea ratio of 2 : 1 only 40% of glycerol conversion was achieved (entry 1) out of a maximum possible conversion of 50%, whereas when more urea is available we achieve 67% conversion (entry 4). More importantly, the selectivity of the reaction gradually changes with the molar ratio of the two reactants, in particular, selectivities to glycerol carbonate now range from 70% (entry 1) to 34% (entry 4). Also, the increase in urea concentration results in an enhancement of the consecutive carbonylation reaction producing **9**, and selectivity to **9** increases from 2% to 22% (entries 1 and 4). The blank reaction carried out with excess glycerol (2 : 1 glycerol : urea molar ratio) also produced less of compound **7** (see Fig. S6 in ESI for full time on line reaction profile†).

Table 2 Catalytic data obtained from an uncatalysed reaction with various glycerol/urea molar ratios

			Selectivity (%)				
Entry	Glycerol : urea (molar ratio)	Conv. (%)	Glycerol carbonate	**5**	**7**	**9**	Glycerol carbonate yield (%)
1	2 : 1	40	70	27	1	2	28
2	1 : 1	57	41	42	7	10	24
3	1 : 1.5	59	36	44	7	13	21
4	1 : 2	67	34	37	9	22	21

[a] Reaction conditions: glycerol/urea molar ratio: 1 : 1.5, temperature: 150 °C, catalyst: 0.25 g, time: 4 h. Product (**5**) = 2,3-dixydroxylpropyl carbamate, product (**7**) = 4-(hydroxymethyl) oxazolidin-2-one, product (**9**) = (2-oxo-1,3-dioxolan-4-yl) methyl carbamate.

Table 3 Comparison between the product distributions obtained from an uncatalysed and catalysed (2.5 wt.% Au/MgO) reaction with a glycerol/urea molar ratio of 2[a]

				Selectivity (%)				
Entry	Catalyst	Time (h)	Conv (%)	Glycerol carbonate	**5**	**7**	**9**	Glycerol carbonate yield (%)
1	Blank	0	0	0	0	0	0	0
		0.5	10	11	78	0	11	1
		1.0	18	25	66	3	6	4
		2.0	29	35	55	5	5	10
		4.0	40	57	37	3	3	23
2	2.5wt%Au/ MgO	0	0	0	0	0	0	0
		0.5	22	20	73	5	2	4
		1.0	30	38	55	5	2	11
		2.0	41	67	31	0.02		28
		4.0	41	85	13	0.02		35

[a] Reaction conditions: glycerol/urea molar ratio: 1 : 1.5, temperature: 150 °C, catalyst: 0.25 g, time: 4 h. Product (**5**) = 2,3-dixydroxylpropyl carbamate, product (**7**) = 4-(hydroxymethyl) oxazolidin-2-one, product (**9**) = (2-oxo-1,3-dioxolan-4-yl) methyl carbamate.

The reaction of glycerol with urea was also carried out using an excess of glycerol in the presence of the 2.5 wt% Au/MgO catalyst (see Fig. S6 in ESI†). Table 3 compares the full time on line conversion and selectivities for the glycerol-rich reactions both in the presence and absence of the catalyst (2.5% Au/MgO). It is remarkable how the selectivity to 2,3-dihydroxypropyl carbamate (**5**) decreases after 4 h reaction from 37% to 13% in the presence of the catalyst. Moreover, hardly any formation of compound (**7**) was detectable when the catalyst was present, thus suggesting that the catalyst is selective to the formation of the carbonate at the expense of the nitrogen insertion products. It also appears that less glycerol carbonate reacts with a second equivalent of urea molecule yielding (2-oxo-1,3-dioxolan-4-yl)methyl carbamate (**9**) in the presence of a catalyst. Comparison of the catalysed and uncatalysed reactions in Table 3 suggests that the major differences in the two reaction profiles is that 2,3-dihydroxypropyl carbamate (**5**) reacts faster to give the desired carbonate in the presence of our catalyst. Overall, for reactions performed with excess glycerol high activity (referred to urea) was found, but the main role of the catalyst appears to be on improving selectivity by promoting glycerol carbonate formation at the expense of other by-products.

Mechanistic considerations and role of the catalyst. In view of these results, we propose that the first step of the reaction proceeds uncatalysed *via* a homogeneous reaction and this first step is very favourable with no evidence of competition with the other possible reaction pathways under our reactions conditions, as neither compounds **4**, **3** nor **11** have been detected by us or in other recent reports.[17,30] The second step of the reaction is however crucial to determine selectivity, and this is precisely where our catalysts are playing a key role. In this second step, 2,3-dihydroxypropyl carbamate (**5**) can form a number of compounds, but only a few were detected. Importantly, the catalyst is more selective to glycerol carbonate than towards 4-(hydroxymethyl)oxazolidin-2-one (**7**), the 6-ring carbonate (**8**) or the insertion of a second urea into the primary OH group of the primary product (**3**). Therefore, it is evident that a general trend exists whereby any of the hydroxyl groups in glycerol may act as nucleophiles, eliminating ammonia, and this is supported by the fact that compounds **5**, **6** and **9** are the only major products of the reaction. Each of these is a product of a nucleophilic attack of a hydroxyl group on the electrophilic carbon in the carbonyl group. The amine group only acts as a nucleophile to eliminate water in very small proportion and only in the second step of the reaction where compound **5** was already formed and the leaving group comes from a secondary carbon. The only primary product detected from the reaction of glycerol with urea was compound **5**, which indicates that the primary hydroxyl group in glycerol is a much better nucleophile than the amine groups in urea. This becomes evident when comparing the $\mathrm{p}K_\mathrm{a}$ of urea (0.10) with that of glycerol (14.15) and considering that a very low $\mathrm{p}K_\mathrm{a}$ is also expected for the intermediate carbamate (**5**).

It is also noteworthy that the 6-membered ring (**8**) was not detected in any of the experiments performed. One might expect that the intramolecular cyclisation reaction of compound (**5**) to form glycerol carbonate (**6**) would compete with the formation of the 6-membered ring isomer (**8**). Both intramolecular cyclisation reactions are classified as *exo*-trig following Baldwin's rules as in both cases the bond broken during the cyclisation step is outside the ring and in both cases the electrophilic carbon is sp2 (trigonal). Following Baldwin's rules both 5 and 6-membered rings should be favourable. In the present case however, the usual preference for 5-ring formation over 6 reaches something of a maximum.

The most favoured hypothesis on the role of catalysts for this reaction is that the catalyst provides a suitable combination of Lewis basicity and acidity.[17] Some authors have implied that the role of the catalyst could be that of co-adsorbing urea and glycerol to favour the formation of glycerol carbonate. However, it has also been shown that the first step of the reaction is very fast and occurs uncatalysed. Careful observation of the preliminary experiments performed in his work leads us to favour that the role of the catalyst is related to the slower second step of the reaction, to the intramolecular reaction forming the carbonate. Gold can interact with carbonate groups as it shows a promotional effect over ceria in the transalkylation of propylene carbonate to dimethyl carbonate, although few analogies can de made for the two reactions.[41] More importantly, there have been a number of reports where gold acts as a good Lewis acid catalyst for organic reactions, and most recently gold salts and complexes have been reported to be excellent Lewis acids for the formation of cyclic acetals from glycerol resulting in the formation of the 5-membered ring dioxolane derivatives.[42] In our particular reaction, the results suggest that the main effect of the catalyst is indeed in promoting the intramolecular reaction of the 2,3-dihydroxypropyl carbamate (**5**) to glycerol carbonate (**6**) which seems a very good candidate for Lewis acid catalysis. Gold might coordinate to the carbonyl group of the reaction intermediate (**5**) and facilitate the nucleophilic attack by the secondary hydroxyl group into the electrophilic carbon. The amine leaving group would then accept the proton from the hydroxyl which releases the ammonia and forces the closure of the ring as a carbonate. The origin of the enhanced selectivity might originate from the absorption of **5** favouring the desired intermolecular interaction that yields glycerol carbonate. The role of the support could be many, and future work will provide new clues whether the support is merely ensuring that gold is in the suitable active state or there are other metal support interaction effects. Previous work in gold catalysis research indicates that the support plays a fundamental role in the activity and selectivity for many other reactions, such as in hydrogen peroxide synthesis where the activity of the metal could be correlated with the isoelectric point of the support utilised.[43] It must be noted that the most basic support was more effective and, we consider that the combination of this with the Lewis acidity of the supported gold results in the improvement in yields and selectivity. This approach is in agreement with the studies by Climent *et al.*[17] and also finds some parallelism with observations that a collaborative effect exists between gold and the support to induce the selective oxidation of alcohols.[44]

Conclusion

A number of heterogeneous catalysts have been discovered to promote the formation of glycerol carbonate from the solvent-free reaction of glycerol with urea. In particular Zn, Ga and Au supported in ZSM-5 promoted the reaction in the following order Au > Ga > Zn. Additionally, a vanadyl pyrophosphate catalyst was also very active. The activity of gold supported on titania, carbon, niobium oxide, zinc oxide and magnesium oxide prepared *via* a simple impregnation technique was evaluated. However, the most active catalysts were obtained when gold was deposited on magnesium oxide and calcined at 400 °C and, the catalyst did not lose its activity even after 10 re-cycles. The yields of glycerol carbonate obtained are superior to those obtained with homogenous zinc sulfate salts previously reported and, the catalyst increases selectivity to glycerol carbonate. This might occur by promoting the intramolecular cyclisation of the carbamate intermediate of the reaction to form glycerol carbonate.

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