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Terms of Use

Highly Efficient and Selective Transformations of Glycerol Using Reusable Heterogeneous Catalysts

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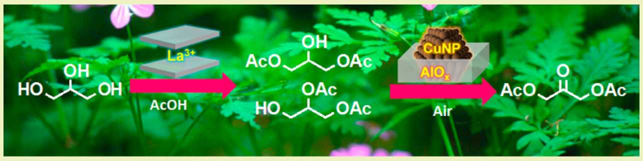
Supporting Information

ABSTRACT: The highly efficient and selective transformations of glycerol to valuable compounds using reusable heterogeneous catalysts are demonstrated. Lanthanum cation-exchanged montmorillonite shows high activity for the selective synthesis of diacetylglycerols through acetylation with acetic acid. Furthermore, the diacetylglycerols obtained can be subsequently oxidized into 1,3-diacetoxyacetone under air using an AlO$_x$-embedded copper nanoparticle catalyst.



KEYWORDS: *Glycerol, Acetylglycerols, Lanthanum-exchanged montmorillonite, Copper nanoparticles, One-pot reaction*

INTRODUCTION

Glycerol is an unavoidable coproduct of the biodiesel production process, and so recent increases in the adoption of biodiesel have led to a concurrent rise in glycerol stocks.[1,2] It would therefore be desirable to develop methods of transforming glycerol into value-added chemicals in order to increase the profitability of biodiesel manufacture. Among the various transformations of glycerol which have been proposed,[3−11] the conversion of glycerol into highly valuable acetylglycerols is promising,[12−16] and the synthesis of diacetylglycerols (DAGs) has received much attention because these compounds are widely applied in the pharmaceutical, cosmetics, polymer, food additives, and tobacco industries, in addition to their role as biodiesel additives.[17,18] To date, many acid catalyst systems have been developed for the production of DAGs.[5,19−23] However, the selectivity for DAGs is still low, and harsh reaction conditions are required. Therefore, there is a demand for the development of highly efficient catalytic systems for the production of DAGs from glycerol that can be applied to industrial-scale processes.[24−32]

Montmorillonite (mont) is a layered clay mineral consisting of silica−alumina sheets with exchangeable Na ions located in the interlayers. Various metal cations can be introduced to the interlayer using ion-exchange techniques, and the expandable nature of the mont interlayers enables reactant molecules to easily access such active metal species.[33] Our previous work has focused on the insertion of various types of active metal species within the mont interlayers, resulting in efficient and unique catalysis, including metal ions,[34−36] metal oxides,[37−39] and metal clusters,[40,41] for the purpose of effective organic transformations.

Herein, we demonstrated the highly efficient and selective transformations of glycerol to valuable compounds using heterogeneous catalysts based on the mont system (Scheme 1). Specifically, lanthanum cation-exchanged mont (La^{3+}-mont) is shown to act as a highly efficient and reusable heterogeneous catalyst for the selective synthesis of diacetylglycerols through acetylation with acetic acid. Furthermore, the diacetylglycerols obtained from this process can be subsequently oxidized into 1,3-diacetoxyacetone with over 99% selectivity using air as an environmentally friendly oxidant through the use of an AlO$_x$-embedded copper nanoparticle catalyst (CuNP@AlO$_x$). These two catalyst systems can also be combined to allow the one-pot synthesis of 1,3-diacetoxyacetone from glycerol, in which each catalyst functions independently without mutual deactivation. Moreover, the CuNP@AlO$_x$ catalyst has also demonstrated the complete monomerization of diacetylglycerol isomers to 1,3-diacetylglycerol via successive oxidation−hydrogenation reactions. Both of these solid catalysts can be separated from the reaction mixture simply by filtration and reused with no significant loss of their initial catalytic activities. The catalyst systems offer the significant advantages of high activity and selectivity, facile preparation, and easy recovery and recycling with excellent reusability. These characteristics are important in the industrial synthesis of value-added glycerol derivatives.

EXPERIMENTAL SECTION

Various metal cation-exchanged monts were prepared according to our previously reported procedure through the treatment of Na$^+$-mont (Kunipia F, Kunimine Industry Co. Ltd.; Na, 2.73; Al, 10.3; Fe, 1.35; Mg, 1.97%) with aqueous solutions of various metal triflates.[34−36] La^{3+}-mont was obtained as a gray powder from this process, and X-ray diffraction studies showed an increase in the interlayer spacing from

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Scheme 1. Transformations of Glycerol to Valuable Compounds Using La^{3+}-mont and CuNP@AlO_x Catalysts

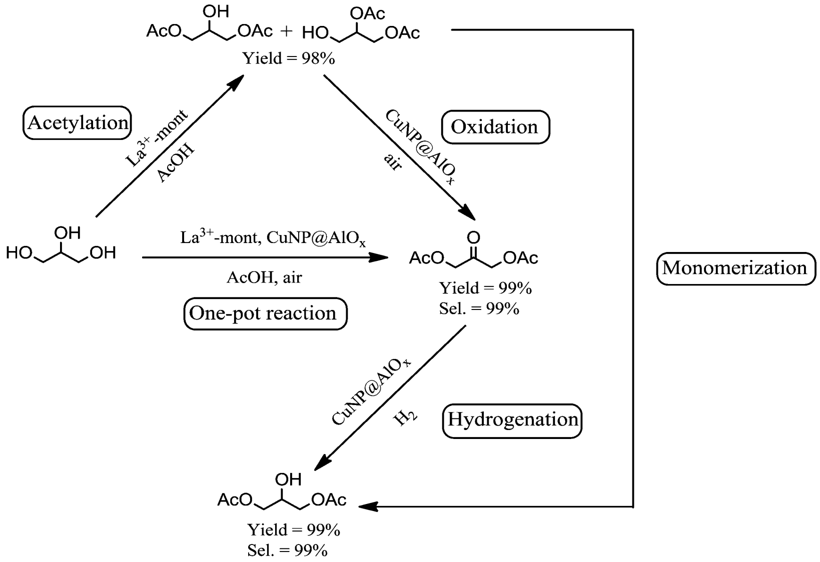
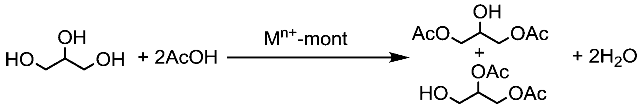


Table 1. Diacetylation of Glycerol with Acetic Acid over Various Metal-Exchanged Mont Catalysts[a]



			selectivity for acetylglycerol (%)[b]		
entry	catalyst	conv. (%)	mono-[c]	di-[d]	tri-
1	La^{3+}-mont	98	0	>99 (2.5)	0
2[e]	La^{3+}-mont	98	0	>99 (2.5)	0
3	Ce^{4+}-mont	98	37 (5.8)	44 (2.5)	19
4	Sc^{3+}-mont	97	37 (6)	43 (2.5)	20
5	Ti^{4+}-mont	85	0	61 (2.5)	39
6	Fe^{3+}-mont	85	0	64 (2.5)	36
7	$La(OTf)_3$	2	trace	1	0
8	Na^{+}-mont	2	trace	1	0

[a] Reaction conditions: glycerol (1 mmol), AcOH (2 mmol), catalyst (metal; 0.02 mmol), toluene (3 mL), 120 °C, and 24 h. [b] Calculated from the isolated yields. [c] Ratio of 1-/2-acetylglycerol by ^1H NMR analysis are in parentheses. [d] Ratio of 1,3-/1,2-diacetylglycerol by ^1H NMR analysis are in parentheses. [e] Fifth reuse experiment.

2.1 to 5.3 Å resulting from the cation exchange. This expanded distance demonstrates that La^{3+} cations were introduced into the mont interlayers by a simple ion-exchange reaction. From elemental analysis data, the La and Na atom loadings were found to be 0.62 and 0.01 wt %, respectively, which indicates that one La^{3+} ion has been substituted for each three equivalents of Na^+ ions. Fourier transform of the k^3-weighted La K-edge extended X-ray absorption fine structure (EXAFS) exhibited a peak at 2.0 Å assigned to the La−O moiety, while no peaks due to the La−(O)−La bond were observed. A curve-fitting analysis showed that the interatomic distance and the coordination number were 2.55 Å and 11, respectively, indicating the La^{3+} species is present within the mont interlayers as a monomeric aqua cation.[42] The CuNP@AlO_x employed in this work was synthesized according to our recent reported method.[43] Details of the reaction procedures are described in the Supporting Information.

RESULTS AND DISCUSSION

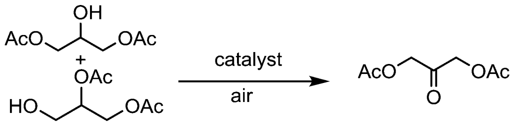
The diacetylation of glycerol with two molar equivalent of acetic acid was carried out using a variety of metal cation-exchanged monts in toluene solvent at 120 °C. Among the monts tested, La^{3+}-mont exhibited the highest catalytic activity, producing 1,3- and 1,2-diacetylglycerol in 98% combined yield with >99% selectivity (Table 1, entry 1). This very high selectivity is unique among the metal cation-exchanged monts tested. The use of other rare earth metals and transition metals within the mont layers, including Ce, Sc, Ti, and Fe, resulted in high conversion values of the glycerol but lower selectivities for the diacetylglycerols (Table 1, entries 3−6). Interestingly, the use of either $La(OTf)_3$ or Na^+-mont, which are the precursors of La^{3+}-mont, resulted in extremely low yields of diacetylglycerols (entries 7 and 8), demonstrating that the insertion of La^{3+} cations into the mont interlayers dramatically changes the catalytic performance of the La^{3+}. The catalytic activity and selectivity of La^{3+}-mont for diacetylglycerol in the diacetylation of glycerol are significantly greater than those of previously reported catalysts such as Niobia/TPA (conv. of glycerol = 97%, sel. for diacetylglycerols = 57%),[44] TPA/Cs_x−ZrO_2 (90% and 54%),[45] K-montmorillonite (96% and 9%),[46] HZSM-5 (30% and 10%),[13] MoO_x/TiO_2−ZrO_2 (100% and 40%),[47] phosphotungstic acid/activated carbon (86% and 63%),[21] and Amberlyst 15 (83% and 60%).[48]

After the completion of the reaction, the La^{3+}-mont catalyst was easily recovered from the reaction mixture by filtration. Furthermore, the used La^{3+}-mont catalyst exhibited excellent reusability with consistently high activity and selectivity even after five consecutive cycles (entry 2). No quantifiable amount of leached La was detected in the filtrate by inductively coupled plasma−atomic emission spectroscopy (ICP-AES) analysis, which is consistent with the high reusability of La^{3+}-mont.

EXAFS analysis was performed to elucidate the atomic structure of the used La^{3+}-mont. Notably, La *K*-edge EXAFS data showed only a single peak at 2.0 Å, assignable to the La−O group, with an interatomic distance and coordination number similar to those of fresh La^{3+}-mont. These results clearly indicate that the monomeric aqua La^{3+} cation species was maintained during the acetylation reaction. This phenomenon is very different from the reported behavior of the aqua complex $[La(H_2O)_x]^{3+}$, which readily undergoes hydrolysis to yield OH-bridged dimers and trimers.[49] The present La^{3+}-mont catalyst possesses highly stable monomeric La aqua species due to the fact that the cations are strongly held within the mont layers, which provides for both high activity and exceptional durability. La^{3+}-mont also offers the unique advantage of interlayer expandability; the interlayer spacing within the La^{3+}-mont expands from 5.3 to 7.4 Å when soaked in a toluene solvent, which allows substrates ready access to the active La ions. The superior catalytic activity of La^{3+}-mont for DAG as compared to other metal catalysts might be attributed to the high coordination number of the La cation. The La cation within the mont layers is capable of dual activation of both the glycerol and the acetic acid reactants through multiple coordination. Moreover, La^{3+}-mont was applicable to the selective synthesis of mono- and triacetylglycerol from glycerol by controlling the amount of acetic acid used. The use of 1 and 3 molar ratios of acetic acid to glycerol provided mono and triacetylglycerol in 97% and >99% yields, respectively.

We next investigated further functionalization of glycerol by the selective oxidation of the remaining hydroxyl group in DAGs to afford diacetoxyacetone. The compound 1,3-diacetoxyacetone can serve as a feedstock for the synthesis of various chemicals and also is a pharmaceutically important precursor for the synthesis of antifungals.[50−53] In an initial screening process, various supported metal nanoparticles known to have catalytic potential for the aerobic oxidation of alcohols were examined.[54−58] The oxidations were carried out at 180 °C for 5 h, using air as a green oxidant, by addition of the metal nanoparticle catalysts to the reaction filtrate following the acetylation. Notably, base metal Cu nanoparticles embedded in an AlO$_x$ matrix (CuNP@AlO$_x$) were found to be the best catalyst among those tested,[43] allowing the complete conversion of DAGs to 1,3-diacetoxyacetone with excellent yield under aerobic conditions (Table 2, entry 1). Other supported Cu nanoparticles also served as selective catalysts for the aerobic oxidation of DAGs to 1,3-diacetyl acetone, but the observed efficiencies were lower than that of CuNP@AlO$_x$ (entries 3−6).[59] Interestingly, the leaching of Cu species out of CuNP@AlO$_x$ was not observed by ICP-AES analysis, while visible leaching was seen with other supported Cu nanoparticle materials, such as Cu/FAP, and Cu/HAP. In addition, recovered CuNP@AlO$_x$ was reusable without any loss of activity or selectivity (Table 2, entry 2). The oxidation of 1,2-DAG proceeds through its isomerization to the more stable 1,3-DAG followed by the oxidation of 1,3-DAG to 1,3-diacetoxyacetone.[60,61] The high efficiency of Cu nanoparticles in this reaction compared to other metal nanoparticles is due to their preferential oxidation ability for secondary hydroxyl groups over primary hydroxyl groups.[62]

Table 2. Oxidation of Diacetylglycerols Using Various Metal Nanoparticle Catalysts[a]

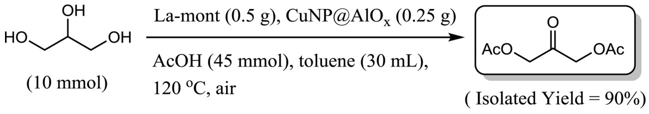


entry	catalyst	conv. (%)[b]	yield (%)[c]
1	CuNP@AlO$_x$	100	99
2[d]	CuNP@AlO$_x$	100	98
3	Cu/Al$_2$O$_3$	70	65
4	Cu/SiO$_2$	65	63
5	Cu/FAP	45	40
6	Cu/HAP	30	25
7	Cu$_2$O	12	8
8	Cu(NO$_3$)$_2$	0	0

[a] Reaction conditions: mixture of 1,2- and 1,3-diacetylglycerol (1.0 mmol), catalyst (Cu: 0.38 mmol), toluene 3 mL, 180 °C, and 5 h. [b] Determined by GC using internal standard. [c] Isolated yields. [d] Third reuse experiment.

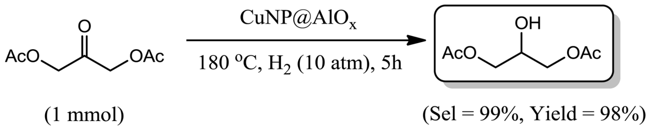
We further attempted the combination of these two heterogeneous catalyst systems in a one-pot synthetic process. The one-pot transformation of glycerol to 1,3-diacetoxyacetone through the acetylation of glycerol followed by the aerobic oxidation of acetylglycerols was investigated, employing both La^{3+}-mont and CuNP@AlO$_x$ under scale-up reaction conditions (Scheme 2). Interestingly, La^{3+}-mont and CuNP@AlO$_x$ were found to work independently without any mutual deactivation, and 1,3-diacetoxyacetone was obtained in excellent yield as the sole product.

Scheme 2. One-Pot Selective Synthesis of 1,3-Diacetoxyacetone from Glycerol under Scale-Up Reaction Conditions



Furthermore, CuNP@AlO$_x$ was shown to act as a bifunctional catalyst in the reversible transformation between 1,3-DAG and 1,3-diacetoxyacetone via a combination of oxidation and hydrogenation.[63] Using this method, 1,3-diacetoxyacetone was successfully converted into 1,3-DAG in 98% yield as the sole product by reaction under a H_2 pressure (Scheme 3). Therefore, the use of CuNP@AlO$_x$ enabled the complete monomerization of the initial mixture of 1,2- and 1,3-DAGs resulting from the acetylation of glycerol to 1,3-diacetylglycerol with 99% selectivity through successive oxidation−hydrogenation reactions. To the best of our knowledge, this is the first example of the selective synthesis of 1,3-diacetylglycerol from glycerol. These transformation reactions show great

Scheme 3. Selective Hydrogenation of 1,3-Diacetoxyacetone to 1,3-Diacetylglycerol Using CuNP@AlO$_x$



promise with regard to allowing efficient utilization of the enormous quantities of glycerol currently produced in biodiesel synthesis, leading to significant improvements in the economic viability of biodiesel production.

CONCLUSION

In conclusion, we have demonstrated the highly efficient and selective transformations of glycerol to oxygenated derivatives using heterogeneous catalysts. La^{3+}-mont and CuNP@AlO_x showed high activity for the acetylation of glycerol and the aerobic oxidation of diacetylglycerols to 1,3-diacetoxyacetone, respectively. The use of these two heterogeneous catalysts in a one-pot reaction process was also applicable to the direct and selective synthesis of 1,3-diacetoxyacetone from glycerol. Moreover, CuNP@AlO_x demonstrated the complete monomerization of diacetylglycerol isomers to 1,3-diacetylglycerol through oxidation−hydrogenation reactions.

ASSOCIATED CONTENT

Supporting Information

Experimental details including catalyst preparation and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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