



Catalytic Oxidation of Allylic Alcohols to Methyl Esters

Gallas-Hulin, Agata; Kotni, Rama Krishna; Nielsen, Martin; Kegnæs, Søren

Published in:
Topics in Catalysis

Link to article, DOI:
[10.1007/s11244-017-0821-1](https://doi.org/10.1007/s11244-017-0821-1)

Publication date:
2017

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Gallas-Hulin, A., Kotni, R. K., Nielsen, M., & Kegnæs, S. (2017). Catalytic Oxidation of Allylic Alcohols to Methyl Esters. *Topics in Catalysis*, 60(17-18), 1380-1386. <https://doi.org/10.1007/s11244-017-0821-1>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Catalytic oxidation of allylic alcohols to methyl esters

Agata Gallas-Hulin^a, Rama Krishna Kotni^a, Martin Nielsen^a and Søren Kegnæs^{a,*}

^aTechnical University of Denmark, Department of Chemistry, 2800 Kgs. Lyngby

* skk@kemi.dtu.dk, +45 45 25 24 02

Abstract:

Aerobic oxidation of allylic alcohols to methyl esters using gold nanoparticles supported on different metal oxide carriers has been performed successfully under mild conditions (room temperature, 0.1 MPa O₂) without significant loss of catalytic activity. The effects of different reaction parameters are studied to find the suitable reaction conditions. All catalysts are characterised by XRD, XRF and TEM. Among these catalysts, Au/TiO₂ showed the most efficient catalytic activity towards the selective oxidation of allylic alcohols to the corresponding esters. Moreover, the same Au/TiO₂ catalyst is used to optimize all the reaction parameters including the significance of the base to promote the reaction. Due to the mild reaction conditions and high conversions as well as selectivity, the utilization of titania-supported gold nanoparticle catalysts represents a benign reaction protocol to synthesize methyl esters from allylic alcohols.

1. Introduction

Over the past decade there has been a strong interest in the alcohol oxidation using gold catalysts [1]. Conventional alcohol oxidation requires toxic metal oxidants and is usually performed at harsh conditions. Although a number of methods have been developed, the search for new facile, cost effective and environmentally benign procedures that can avoid the use of large excess of toxic and

23 expensive stoichiometric metal oxidants has attracted significant interest [2, 3]. Development of
24 environmentally-friendly catalytic reaction is a crucial part, in particular with respect to the production
25 of fine chemicals. The selective oxidative esterification of alcohol is a key reaction used to produce
26 numerous important chemical intermediates and commodity chemicals [4]. Oxidation with molecular
27 oxygen represents a green and sustainable oxidation method and, therefore, has attracted increasing
28 attention over recent years [5, 6]. Furthermore, over the past decade, gold has been identified as an
29 active catalyst in a variety of reactions, in particular in the selective oxidations of alcohols to its
30 corresponding carbonyl compounds such as aldehydes, carboxylic acids and esters [7-10].
31 Recent literature shows a growing amount of fundamental research performed with selective alcohol
32 oxidation [11-19]. In particular oxidative esterification of alcohol to methyl esters is one of the good
33 examples of aerobic oxidation reactions leading to the formation of methyl esters which are important
34 in organic chemistry as they are reasonably stable and can be transformed to several other functional
35 groups [20-25]. Among others, allyl alcohol has a particular importance as a potential starting material
36 for the production of acrylic acid or its methyl ester which are widely used for the production of
37 superabsorbent polymers [26]. Christensen et al. oxidized acrolein – aldehyde of allyl alcohol, in
38 methanol under oxygen atmosphere using commercial gold supported on zinc oxide, producing methyl
39 acrylate with 87% selectivity at 97% conversion [27]. Rossi et al. oxidized allyl alcohol in water at
40 room temperature using commercial Au/TiO₂ giving 3-hydroxypropionic acid and acrylic acid with
41 yields 8% and 23.5%, respectively [28]. Yamakawa et al. used various metal oxides and zeolites in
42 hydrogenation of allyl alcohol in methanol with the main product being 3-methoxy-1-propanol at yields
43 of approximately 80% [29].

44

45 **FIGURE 1**

46 Here we present a new method for the synthesis of methyl esters directly via the selective oxidation of
47 allylic alcohols using molecular oxygen as a terminal oxidant at room temperature. Aerobic oxidation
48 of allyl alcohol (AA) in methanol yielding methyl esters i.e. methyl acrylate (MA) and methyl 3-
49 methoxypropionate (MMP) tested with gold nanoparticles stabilized on different metal oxides as
50 support materials (Al_2O_3 , CeO_2 , ZrO_2 , and TiO_2), see Figure 1. Among all the examined catalysts,
51 commercial Au/ TiO_2 catalyst reached the best performance, affording a quantitative combined yield of
52 MA and MMP after 24 h. Therefore, further reaction conditions, such as base loading, choice of base,
53 substrate concentration, heterogeneity of the reaction, and reusability of the catalyst, are studied with
54 Au/ TiO_2 as catalyst. The morphological studies of the catalysts were performed by XRD, XRF, TEM
55 and nitrogen physisorption. Quantitative analysis of conversion of allyl alcohol is achieved by GC.

56

57 **2. Experimental**

58 **2. 1. Materials**

59 All the chemicals used for the study are purchased from commercial sources and are used without
60 further purification: allyl alcohol (99%, Aldrich), benzyl alcohol (99%, Aldrich), cinnamyl alcohol
61 (98%, Aldrich), 2-methyl-2-propen-1-ol (99%, Aldrich), trans-2-penten-1-ol (95%, Aldrich), methanol
62 (99.5%, Aldrich), mesitylene (98%, Aldrich), potassium methoxide (25% in methanol, Aldrich),
63 sodium hydroxide (98%, Aldrich), sodium methoxide (30% in methanol, Fluka), methyl acrylate (99%,
64 Aldrich), methyl methoxy propionate (99%, Aldrich) chloroauic acid (III) (99.9%, Aldrich), titanium
65 oxide (99.7%, Aldrich), cerium oxide (99.5%, Alfa Aesar), aluminum oxide (Riedel-De Haenag
66 Seeize-Hannover), zirconium oxide (96%, Aldrich), Au/ TiO_2 provided by Mintek, referred as a
67 commercial catalyst. The commercial and the synthesized Au/ TiO_2 catalysts had similar catalytic
68 properties, and the following results shown are from the commercial catalyst.

69 **2.2 Preparation of 1 wt% gold catalysts on different supports:** 0.02 g of $\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$ is dissolved
70 in 5 mL of water under stirring until homogeneous yellow solution is obtained. Next, saturated solution
71 of sodium bicarbonate is added dropwise until the mixture reached pH 9. After, 0.99 g of support is
72 added and the mixture is left for 1 h under stirring at 50 °C. During this time the solution gradually
73 shifted color from yellow to colorless. After one hour the suspension is filtered and the catalyst is
74 washed with distilled water until no Cl^- ions are detected by addition of AgNO_3 solution to the filtrate.
75 Finally the recovered material is dried in air for 24 h and then reduced in 10% H_2 in N_2 at 350 °C for 2
76 h with a heating ramp of 5 °C/min.

77 **2.3. Catalyst characterization:** The analysis of catalyst morphology is examined using transmission
78 electron microscopy (TEM) performed on Tecnai T20 G2 operating at 200 kV. The size of the
79 nanoparticles was calculated from measurements of around 100 particles. Images were taken from
80 several different parts of the samples and at different magnifications.

81 Crystal analysis is performed by XRD on Huber G670 with $\text{CuK}_{\alpha 1}$ radiation for 10 min. The nature of
82 gold species and loading of gold on the support material are determined by XRF analysis on
83 PANalytical Epsilon3-XL.

84 Nitrogen gas physisorption analysis was performed at 77 K on a Micromeritics ASAP 2020. The
85 surface area was calculated by the Brunauer-Emmett-Teller (BET) method and the pore size
86 distribution were calculated by the Barrett-Joyner-Halenda (BJH) based on the isotherm desorption
87 branch. The total pore volume were determined from the isotherm adsorption branch by a single point
88 read at around $P/P_0=0.99$.

89 **2.4. Catalytic oxidation of allyl alcohol:** All reactions are performed on a Radleys carousel in ambient
90 conditions under stirring and oxygen flow. In a typical experiment, a 20 mL glass vessel is loaded with
91 50 mg of fractionated catalyst (180-355 μm), 2 mmol of allyl alcohol (130 μL), 148 mmol of methanol

92 (6.0 mL), 0.2 mmol of mesitylene (28 μ L) used as internal standard, and 60 μ L of potassium
93 methoxide. Samples from the reaction are taken at intervals 0 h, 2 h, 5 h, 24 h, and analyzed using GC
94 (Agilent 7890A).

95

96 **3. Results and Discussion**

97 *3.1. Catalysts characterisation*

98 The XRD analysis of gold on titania catalyst used in the study revealed no characteristic reflexes of
99 gold, what can be seen on Figure 2a. This indicates a uniform distribution and a small size of gold
100 nanoparticles on the surface of titania. The XRD patterns of Au/ZrO₂, Au/CeO₂, and Au/Al₂O₃
101 catalysts revealed, similar to Au/TiO₂ no reflexes of gold. XRD patterns of the Au/ZrO₂, Au/CeO₂, and
102 Au/Al₂O₃ catalysts can be found in Figure S1 in the Supplementary Information. The XRD analysis of
103 the TiO₂ shows the presence of a mixture of anatase and rutile phases (~80% anatase, ~20% rutile).
104 TEM analysis of Au/TiO₂ catalyst showed gold particles of size 2-3 nm, evenly distributed on the
105 support without any tendency to form large clusters, as shown in Figure 2b. TEM analysis of Au/ZrO₂
106 and Au/CeO₂ revealed similar sizes of the gold nanoparticles and uniform distributions. The size of
107 gold particles in the Au/Al₂O₃ catalyst is slightly larger (5-10 nm). TEM images of the Au/ZrO₂,
108 Au/CeO₂, and Au/Al₂O₃ catalysts can be found in Figure S2 in the Supplementary Information. An
109 overview of the particle sizes for the different catalysts are shown in Table 1. Additional nitrogen
110 physisorption data are shown in the Supplementary Information, Table S1. The BET Surface areas and
111 pore volumes are as expected for metal oxide supports. XRF analysis of the amount of metallic gold on
112 the support revealed the gold loading equal to 0.98-1wt% for all investigated catalysts. Moreover, no
113 characteristic peaks of chlorine are observed in the spectrum indicating the purely metallic form of gold
114 supported on titania (Figure S4). The nature of the supported gold nanoparticles synthesized by

115 deposition–precipitation has previously been studied in the literature [30]. Details about the
116 characterization of Au/ZrO₂, Au/CeO₂, and Au/Al₂O₃ catalysts using XRD, TEM, XRF and nitrogen
117 physisorption data can be found in the Supplementary Information.

118

119 **FIGURE 2**

120

121 *3.2. Catalytic activity*

122 In order to examine the activity of the gold catalysts deposited on different support materials (ZrO₂,
123 CeO₂, TiO₂, Al₂O₃,) the oxidation reaction of allyl alcohol is performed at 25 °C and 0.1 MPa O₂ with
124 10% of the base CH₃OK. Results from the conducted experiments are shown in Table 1. The best
125 results are obtained with Au/TiO₂ which reached 99% conversion after 24 h with the yield towards
126 MMP of 85%. After 24 h the Au/Al₂O₃ catalyst showed the lowest catalytic activity. This could be due
127 to the larger size of the gold particles in the Au/Al₂O₃ catalyst. The size of the gold particles is
128 comparable for the Au/ZrO₂, Au/CeO₂ and Au/TiO₂ catalysts. Surprisingly, the Au/ZrO₂ and the
129 Au/CeO₂ catalysts showed lower activities than the Au/TiO₂ after 24 h. Especially, since the Au/CeO₂
130 catalyst is known in the literature to be a very active oxidation catalyst even without base. However,
131 the morphology of CeO₂ support is known to play an important role on the catalytic activity. Corma et
132 al. have previously reported that Au/TiO₂ can be a more active than gold on conventional non-
133 nanocrystalline CeO₂ in the oxidation of 3-octanol [16]. Corma et al. also showed that gold supported
134 on nanocrystalline CeO₂ was more active than gold supported on non-nanocrystalline CeO₂ [16].
135 Next, the role of gold in oxidation of allyl alcohol is investigated. A control experiment is performed in
136 which TiO₂ is used as a catalyst. After 24 h no conversion of allyl alcohol is detected (Table 1)
137 confirming the crucial role of gold in the oxidation reaction. The conversion of allyl alcohol to MA and

138 then to MMP is shown in Figure 3. The suggested sequential product formation with MA as an
139 intermediate towards MMP is based on the classic Michael addition, which is favored under, for
140 example, alkaline activation of the nucleophile. However, too high base concentration might shift the
141 equilibrium towards MA and polymerisation through an E1cb intermediate, as shown in Figure 4. As
142 such, MA and MMP are interconvertible.

143

144 **TABLE 1.**

145

146 **FIGURE 3**

147

148 **FIGURE 4**

149

150 To get more insight in to the role of base, a set of reactions with different types of bases is performed
151 with Au/TiO₂. All three examined bases are able to drive the reaction successfully, potassium
152 methoxide showed slight superiority (Table 2). The effect of base amount on the oxidation of allyl
153 alcohol is studied by conducting a series of experiments using different loadings of CH₃OK i.e. 0, 5,
154 10, 15, 20, 50 and 100% under the same reaction conditions. Base is known to assist the oxidation of
155 alcohols on gold supported on titania [31]. Figure 5a depicts the results obtained with different base
156 loadings. The highest yield of MMP is observed for the reaction with 10% of base. When the reaction
157 is performed with increasing base amount, the yield of MMP is observed to be decreasing (19%)
158 gradually. On the other hand, the yield of MA is increased up to approximately 30%. Moreover, the
159 total combined yield of MMP and MA is observed to decrease from quantitative to approximately 50%.

160 Large amounts of base could facilitate polymerization of MA leading to compounds with high
161 molecular weights which are not detected by GC-MS, see Figure 4.

162

163 **TABLE 2**

164

165 **FIGURE 5**

166

167 The effect of substrate to solvent ratio is studied as well. The reaction is performed using different
168 ratios of allyl alcohol to methanol. Data obtained for these experiments is shown in Figure 5b. The
169 highest yield is obtained for substrate to solvent ratio of 1:74 giving 88% yield of MMP after 24 h. It
170 was shown that increasing excess of methanol in the reaction leads to a gradual decrease in the yield of
171 MMP down to 57% with a slight increase in the yield of MA (29%). The possible explanation of this
172 behavior might be the lowered total concentration of base in the reaction mixture for the systems with
173 increased amount of methanol. The mechanism for the formation of allyl alcohol coupling with
174 methanol on an O-activated Au surface has previously been studied by C. M. Friend et al. [32]. The
175 results showed that the product selectivity could be tuned with the concentration of the unsaturated
176 alcohol and methanol.

177 The reusability of the catalyst is examined by performing several reaction cycles with the same
178 catalyst. After each catalytic cycle, the catalyst is filtered, washed with methanol, dried in air for 24 h,
179 and used in the new reaction cycle. After the fourth cycle, the catalyst is additionally reduced in 10%
180 formier gas at 350 °C for 2 h. Data from these experiments is shown in Figure 6a. It is visible, that the
181 conversion of allyl alcohol decreased with the number of runs from 99% in the first run to 91% in the
182 fourth run. A similar but more significant pattern is observed for the yield of MMP which decreased

183 from 87% to 48%. On the contrary, the yield of MA increased from 13% to 38%. The total combined
184 yield of MMP and MA is observed to decrease from quantitative to approximately 86% after the fourth
185 run. In the fifth run, when the regenerated catalyst is used, the activity of the catalyst is recovered
186 giving the yields of the products identical those in the first run. The reason for the drop of activity of
187 the catalyst might be due to the formation of carboxylic acid [31], since no morphological changes in
188 the catalyst or size of gold nanoparticles are observed from TEM analysis, as shown in Figure S3 in
189 Supplementary Information.

190 In order to study the heterogeneity of the reaction, the catalyst is removed from the reaction mixture
191 after 5 h, while all the other parameters remained unchanged. Filtering off the catalyst resulted in
192 inhibition of the reaction with no increase in yield of any of the products after 24 h, which is shown in
193 Figure 6b. This means that even if case of leaching of gold particles from the support material, the
194 activity of the catalyst for the oxidation of allyl alcohol comes from the interaction of gold particles
195 with titanium oxide, and not gold species alone that could leach out of the support into the solution.
196 Furthermore, no gold was observed in the solution by XRF analysis, see Figure S5 in Supplementary
197 Information.

198

199 **FIGURE 6**

200

201 Having established the optimal reactions conditions, a scope of the reaction is examined (Table 3). In
202 addition to allyl alcohol, both alkyl and aryl alkene substituted substrates undergo conversion to the
203 desired products in high yields. As such, conducting the reaction with 2-isobutenol afforded the
204 corresponding ester product in a quantitative combined yield (entry 2), and a combined yield of 86% is

205 obtained with cinnamyl alcohol (entry 3). In addition, employing simply benzyl alcohol also resulted in
206 a quantitative yield of methyl benzoate (entry 4).

207 Comparing entry 1 with entries 2 and 3, selectivity changes from predominantly favoring the methoxy
208 product in entry 1 to favoring the unsaturated products in the other product mixtures. This is not
209 surprising considering the alkene stabilization effects of both σ -donation and hyperconjugation of the
210 methyl substituent (entry 2) and of π -system conjugation (entry 3) towards nucleophilic attack of the
211 methoxide anion.

212

213 **TABLE 3**

214

215 **5. Conclusions**

216 In summary, we reported a feasible and efficient way to oxidize allylic alcohols to its methyl esters
217 using gold nanoparticles supported on different metal oxides as catalysts and with oxygen as oxidant at
218 ambient conditions. The study showed superior activity of Au/TiO₂ over the other synthesized
219 catalysts. The reaction parameters, such as base loading, kind of base, substrate concentration,
220 reusability and homogeneity of the reaction are studied. They revealed the high dependence of
221 selectivity of the reaction on the specific reaction parameters. Due to high conversions and high
222 selectivities achieved in the study, gold supported on titania operating at ambient conditions represents
223 a promising and environmentally-friendly approach for oxidation of allylic alcohols to its methyl esters.

224

225 **6. Acknowledgments:** The authors gratefully acknowledge the support of the Danish Council for
226 Independent Research, Grant No. 12-127580, the support of the Lundbeck Foundation

227 (Lundbeckfonden), Grant No. R141-2013-13244 and the support from VILLUM FONDEN research
228 grant (13158).

229

230 **7. References**

231 1. Della Pina C, Falletta E, Rossi M, (2012) Chem. Soc. Rev. 41: 350-369

232 2. Dijksman A, Marion-Gonzalez A, Payeras A M, Arends I W C E, Sheldon R A (2001) J. Am. Chem.
233 Soc. 123: 6826

234 3. Liu R, Liang X, Dong C, Hu X (2004) J. Am. Chem. Soc. 126: 4112

235 4. Oliveira R L, Kiyohara and Liane P K, Rossi M (2009) Green Chem. 11: 1366

236 5. Mallat T, Baiker A, (2004) Chem. Rev. 104: 3037

237 6. Kon Y, Usui Y, Sato K (2007) Chem.Comm. 4399

238 7. Haruta M, Kobayashi T, Sano H, Yamada N, (1987) Chem. Lett. 16: 405

239 8. Davies S E, Ide M S, Davis R J (2013) Green Chem 15: 17-45

240 9. Højholt K T, Laursen A B, Kegnæs S, Christensen C H (2011) Top. Catal. 54: 1026-1033

241 10. Mielby J, Abildstrøm J O, Wang F, Kasama T, Weidenthaler C, Kegnæs S (2014) Angew Chem.
242 Int. Ed. 53: 12513-12516

243 11. Ryabenkova Y, Miedziak P. J, Dummer N F, Taylor S H, Dimitratos N, Willock D J, Bethell D,
244 Knight D W, Hutchings G J (2012) Top Catal 55: 1283-1288

245 12. Abad A, Almela C, Corma A, Garcia H (2006) Tetrahedron 62: 6666-6672

246 13. Zhang Z, Xin L, Qi J, Wang Z, Li W (2012) Green Chem. 14: 2150-2152

247 14 Yang H, Cui X., Deng Y, Shi F, (2014) RCS Adv. 4: 59754-59758

248 15. Hackett S F J, Brydson R M, Gass M H, Harvey I, Newman A D, Wilson K, Lee A F (2007)

249 Angew. Chem. Int. Ed. 46: 8593-8596

- 250 16. Abad A, Concepcion P, Corma A, Garcia H (2005) *Angew.Chem. Int.Ed* 44: 4066
- 251 17. Christensen C H, Jørgensen B, Rass-Hansen J, Egeblad K, Madsen R, Klitgaard S K, Hansen S M,
252 Hansen M R, Andersen H C, Riisager A (2006) *Angew. Chem. Int. Ed.* 45: 4648-4651
- 253 18. Zope B N, Hibbitts D D, Neurock M, Davis R J (2010) *Science* 330: 74-78
- 254 19. Kumar R, Gravel E, Hagege A, Li H, Jawale D V, Verma D, Namboothiri I N N, Doris E, (2013)
255 *Nanoscale*, 5: 6491-6497
- 256 20. Zheng Su F, Mei Liu Y, Wang L-C, Cao Y, Yong He H, Nian Fan K (2008) *Angew. Chem.* 120:
257 340.
- 258 21. Abad A, Almela C, Corma A, Garcia H (2006) *Chem.Commun.* 3178-3180
- 259 22. Miyamura H, Yasukawa T, Kobayashi S (2010) *Green Chem.* 12: 776-778
- 260 23. Kegnæs S, Mielby J, Mentzel U V, Jensen T, Fristrup P, Riisager A (2012) *Chem. Commun.* 48:
261 2427-2429
- 262 24. Mielby J, Kegnæs S, Fristrup P (2012) *ChemCatChem* 4: 1037-1047
- 263 25. Mielby J, Riisager A, Fristrup P, Kegnæs S (2013) *Catal. Today* 203: 211– 216
- 264 26. [https://ilbioeconomista.com/2013/07/08/basf-cargill-and-novozymes-realize-another-step-towards-](https://ilbioeconomista.com/2013/07/08/basf-cargill-and-novozymes-realize-another-step-towards-the-biobased-economy/?goback=%2Egde_105359_member_256107668)
265 [the-biobased-economy/?goback=%2Egde_105359_member_256107668](https://ilbioeconomista.com/2013/07/08/basf-cargill-and-novozymes-realize-another-step-towards-the-biobased-economy/?goback=%2Egde_105359_member_256107668)
- 266 27. Marsden C, Taarning E, Hansen D, Johansen L, Klitgaard S K, Egeblad K, Christensen C H (2008)
267 *Green Chem.* 10: 168
- 268 28. Della Pina C, Falletta E, Rossi M (2009) *ChemSusChem* 2: 57-58
- 269 29. Yamakawa T, Takizawa M, Ohnishi T, Koyama H, Shinoda S (2001) *Catal. Comm.* 2: 191-194
- 270 30. Zanello R, Delannoy L, Louis C (2005) *Appl. Catal. A* 291: 62–72
- 271 31. Klitgaard S K, DeLaRiva A T, Helveg S, Werchmeister R M, Christensen C H (2008) *Catal. Lett.*
272 126: 213-217

273 32. Zugic B, Karakalos S, Stowers K J, Biener M M, Biener J, Madix R J, Friend C M (2016) ACS

274 Catal. 6: 1833–1839

275

276

277

278

279 **Figure 1.** Depiction of the oxidation of allyl alcohol (AA) in methanol with oxygen at room
280 temperature to methyl esters: methyl acrylate (MA) and methyl 3-methoxypropionate (MMP), using a
281 supported gold catalyst.

282

283 **Figure 2. (a)** XRD pattern of the Au/TiO₂ catalyst; red crosses indicate the positions where the
284 characteristic reflexes of gold occur, which are not observed for the tested catalyst; **(b)** TEM image of
285 Au/TiO₂ catalyst used in the study.

286

287 **Table 1.** Results from oxidation of allyl alcohol using different catalysts with 0.1 MPa of O₂ and room
288 temperature.

289

290 **Figure 3.** Conversion of allyl alcohol (AA) to methyl acrylate (MA) and methyl 3-methoxypropionate
291 (MMP) as a function of time catalyzed by Au/TiO₂, 10% CH₃OK, 0.1 MPa O₂ at room temperature.

292

293 **Figure 4.** Detailed mechanism of sequential product formation from MA to MMP based on the classic
294 Michael addition reaction.

295

296 **Table 2.** Results from oxidation of allyl alcohol using 50 mg of Au/TiO₂ as catalyst with 0.1 MPa of
297 O₂ and room temperature.

298

299 **Figure 5. (a)** Yields of MA and MMP obtained in the oxidation of allyl alcohol with different base
300 (CH₃OK) loadings at ambient conditions with 0.1 MPa O₂; **(b)** The yields of MA and MMP after 24
301 hours of the oxidation of allyl alcohol at different allyl alcohol to methanol ratios using standard
302 reaction conditions.

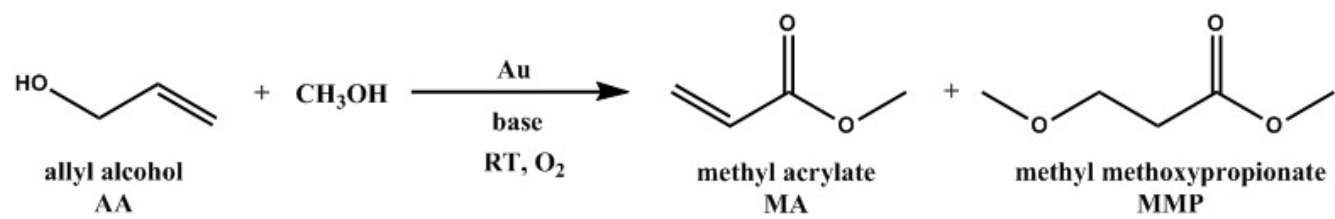
303 **Figure 6.** (a) Conversion of allyl alcohol into methyl acrylate and methyl methoxypropionate in four
304 cycles using recycled catalyst; in the fifth cycle, the catalyst is regenerated by reduction in 350 °C with
305 10% formier gas; (b) Change of conversion of allyl alcohol catalyzed by commercial Au/TiO₂ to its
306 corresponding esters at ambient conditions with 0.1 MPa O₂ and 10% CH₃OK as a function of time for
307 the system with catalyst and after removal of catalyst after 5 h.

308

309 **Table 3.** Results from oxidations of different allylic alcohols using Au/TiO₂ at standard conditions with
310 10% CH₃OK after 24h.

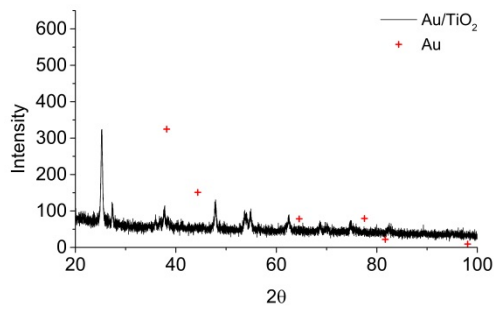
311

312 **Figure 1.**

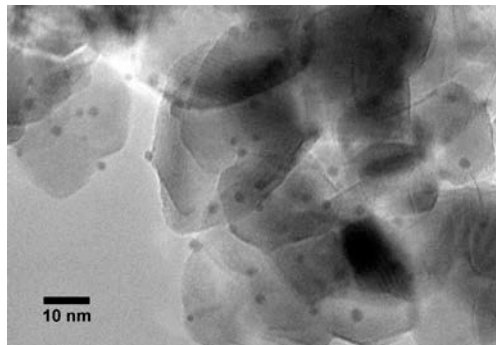


315 **FIGURE 2**

316



a)



b)

317

318

319 **Table 1**

320

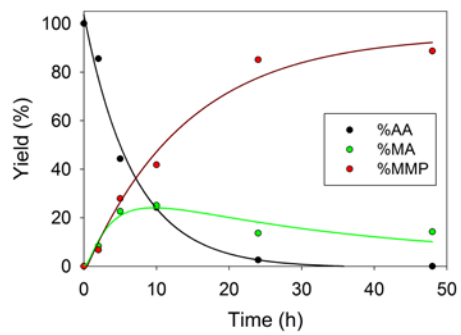
Catalyst ¹	Particle size (nm) ²	Conversion (%) ³		
		2 h	5 h	24 h
Au/ZrO ₂	2-3	3	11	35
Au/CeO ₂	2-3	10	9	35
Au/Al ₂ O ₃	5-10	5	11	22
Au/TiO ₂	2-3	18	33	99
TiO ₂	-	0	0	0

321 ¹ 50 mg of catalyst and 10% of base (with respect to allyl alcohol) is used; ² obtained from TEM322 analysis; ³ obtained from GC analysis.

323

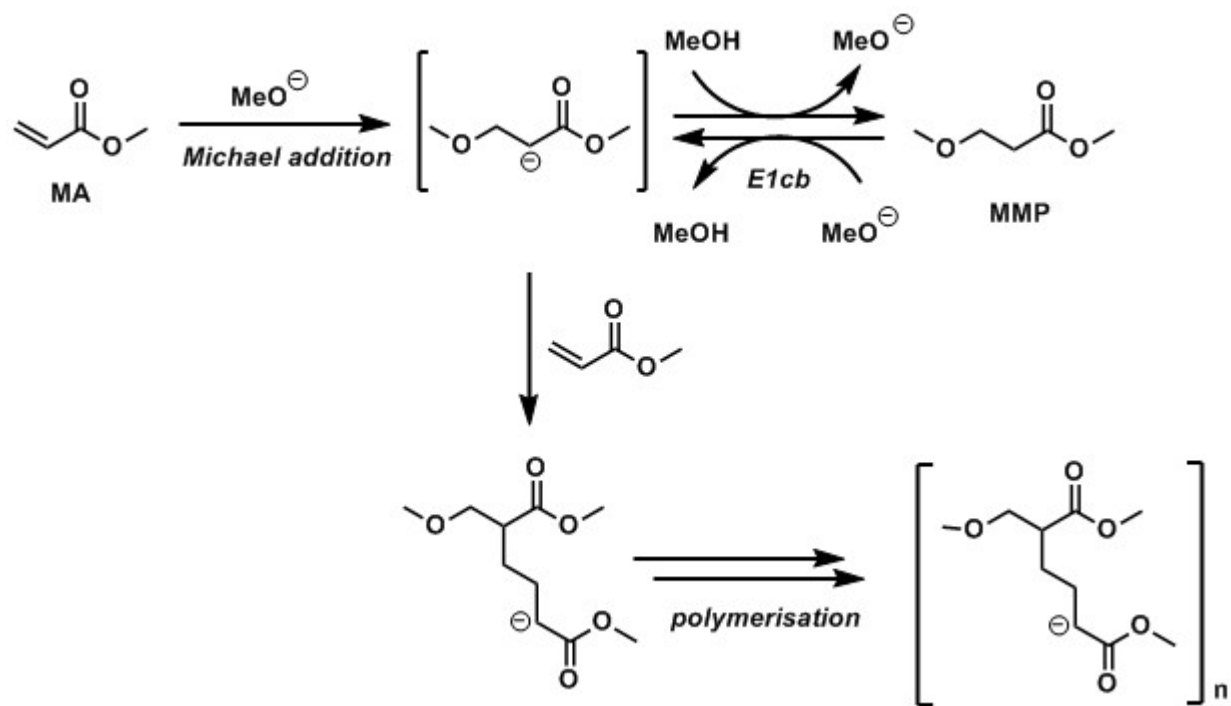
324

325 **Figure 3:**



326

327 **Figure 4**



328

329

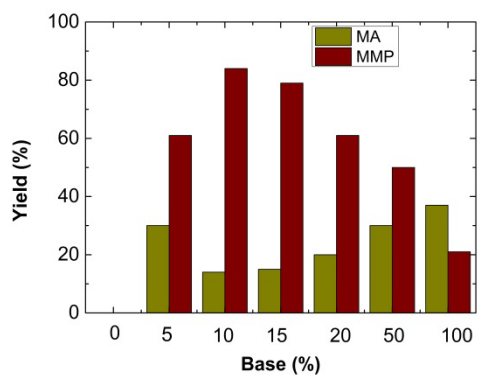
330 **Table 2**

Base¹	Yield³ of MMP at 2 h (%)²	Yield³ of MMP at 5 h (%)²	Yield³ of MMP at 24 h (%)²
CH ₃ OK	7	28	85
CH ₃ ONa	7	17	72
CH ₃ CH ₂ ONa	7	17	82

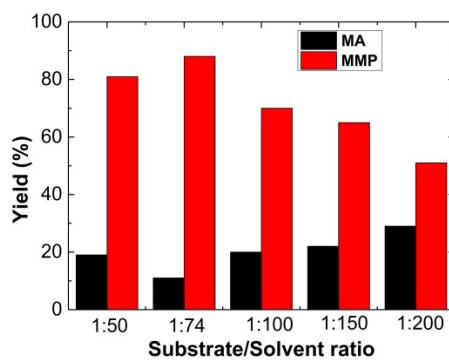
331 ¹10% of base (with respect to allyl alcohol); ²results obtained from GC analysis.

332

333 **Figure 5**



a)

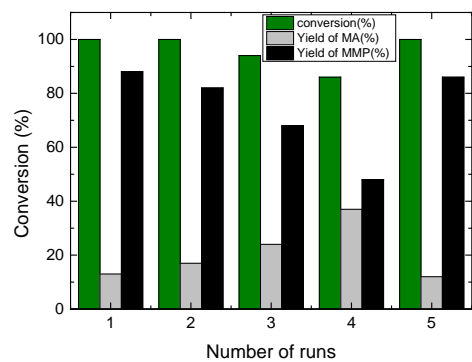


b)

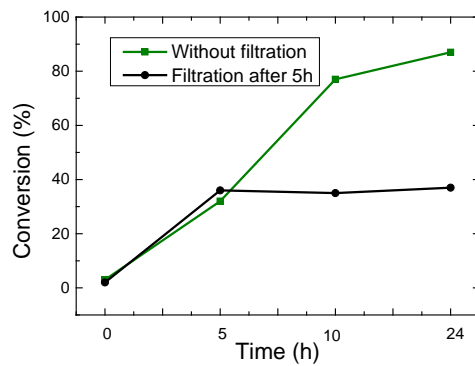
334

335

336 **Figure 6**



(a)

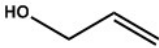
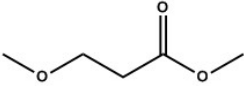
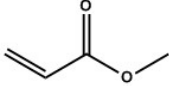
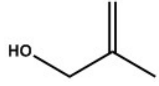
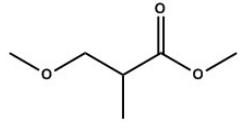
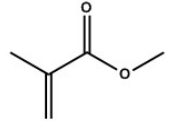
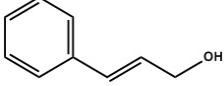
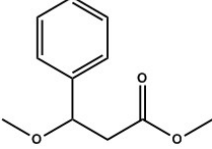
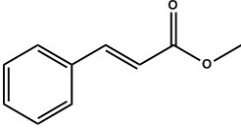
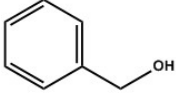
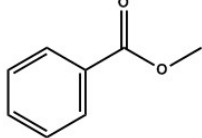


(b)

337

338

339 **Table 3**

Substrate	Product A	Product B	Conversion (%)	Yield A-B (%)
			99	85 - 15
			100	24 - 76
			100	7 - 79
	none		100	n/a - >99

340