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Synthesis of Formic Acid from Monosaccharides Using Calcined Mg-Al Hydrotalcite as Reusable Catalyst in the Presence of Aqueous Hydrogen Peroxide

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Supporting Information

ABSTRACT: Formic acid (FA) can be synthesized from monosaccharides such as glucose, galactose, xylose, arabinose and lyxose by using both calcined Mg-Al hydrotalcite as a solid catalyst and aqueous H_2O_2 as an oxidant in ethanol solvent at 343 K for 5 h. For the glucose oxidation, the FA yield and H_2O_2 utilization efficiency reach 78% and 100%, respectively. The used hydrotalcite catalyst can be easily separated from the reaction mixture and is reusable at least twice.

INTRODUCTION

Formic acid (HCOOH, FA) has attracted much attention as a hydrogen storage organic molecule because FA can be converted into H_2 and CO_2 using catalysts.[1−6] FA is a stable liquid at room temperature (bp 374 K) and is nontoxic and nonflammable, which enables easy handling, and it can be used for various reductive transformations of organic compounds as a hydrogen source.[7−13]

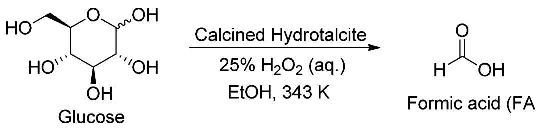
The fermentations of saccharides are the key process for FA synthesis;[14] however, they are expensive because of product purification and strict control of reaction conditions (pH and temperature). Industrially, FA has been produced from a CH_3ONa-mediated carbonylation of CH_3OH under pressurized CO (40 MPa) to form methyl formate, followed by its hydrolysis with excess water.[15] It has also been reported that FA can be obtained from H_2 and CO_2 using homogeneous metal catalysts under pressurized conditions (4−18 MPa).[16−20]

Utilization of biomass-based materials as a renewable resource of valuable chemicals such as fuel and polymer has been extensively reported using solid catalysts.[21−26] Accordingly, the biomass-based FA productions from cellulosic biomass such as saccharides (sugars or carbohydrates) are attractive systems,[27−34] which will open up the way to an indirect utilization of solar energy via plants.

In 1974, Isbel and Naves communicated formation of FA using alkaline hydrogen peroxide from saccharides via an oxidation mechanism by OOH^- species.[33] A research group of Enomoto has strikingly reported the FA synthesis from carbohydrates under hydrothermal conditions at 523 K in the presence of concentrated H_2O_2 and NaOH, where the maximum FA yield was 70%.[29,31] Wölfel et al. demonstrated the oxidation of saccharides with pressurized O_2 (3 MPa) at 353 K for 26 h in water using a Keggin-type polyoxometalate catalyst, $H_5PV_2Mo_{10}O_{40}\cdot 35H_2O$, to yield ca. 50% FA.[30] An acidic Amberlyst-70 could convert cellulose to FA with 53% yield in water at 453 K for 50 h under 0.3 MPa of Ar.[28]

Recently, we reported the conversions of glucose or xylose using CuO_x/MgO catalyst, hydrothermally prepared with cetyltrimethylammonium bromide as a capping agent, in the presence of aqueous (aq) H_2O_2 at 393 K, which gives FA with 65−70% yields (12 h).[27] In continuation of our work, we hereby demonstrate the FA synthesis from various monosaccharides using calcined Mg-Al hydrotalcite[35−42] as a simple and reusable catalyst in the presence of aq H_2O_2 in ethanol solvent at 343 K with an excellent H_2O_2 utilization efficiency (Scheme 1).

Scheme 1. Synthesis of Formic Acid (FA) by Oxidation of Glucose Using Calcined Mg-Al Hydrotalcite Catalyst in the Presence of Aqueous H_2O_2 in Ethanol Solvent



EXPERIMENTAL SECTION

Hydrotalcite (HT, Mg/Al = 5.4) was supplied from Tomita Phamaceutical Co. Ltd. as AD500PF (particle size; 6.4 μm, and surface area; 57 $m^2\ g^{-1}$). The layered structure was confirmed by a powder XRD measurement. D-Glucose, FA, aq H_2O_2, CaO and γ-Al_2O_3 were supplied from Wako Pure Chem Co. Ltd.. D-Fructose, D-xylose, D-galactose, dehydrated ethanol, *N,N*-dimethylformamide (DMF), MgO, ZrO_2 and TiO_2 were purchased from Kanto Chem. Co. Inc.. The Catalyst Society of Japan supplied proton-forms of ZSM-5 (Si/Al = 45, JRC-Z5-90H) and β-type (Si/Al = 12.5, JRC-Z-Hβ 25) zeolites. D-Arabinose and D-lyxose were supplied from Acros Organics and Tokyo Chemical Ind. Co. Ltd., respectively. SiO_2, SrO, Amberlyst-15 and Amberlyst-A26(OH) were purchased from Sigma-Aldrich Co. Ltd..

In a typical reaction procedure, glucose (0.56 mmol) was weighed in a 50 mL Schlenk tube, followed by the addition of calcined HT (0.1 g). The HT was calcined in air at 723 K for 5 h at a ramp rate of 10 K min^{-1}, which converts the layered structure of HT into well mixed Mg-Al oxides possessing an

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acid−base bifunctional surface.[42] Thereafter, ethanol (5 mL) and aq H_2O_2 (2.8 mmol) were added in the Schlenk tube and a N_2 flow was maintained. The solution was stirred at 343 K for 5 h to achieve a high glucose conversion. After the reaction, the reactants were allowed to cool down to room temperature for 20 min. The resultant reaction mixture was diluted to 20 times with water, and the catalyst was filtered off using a Milex syringe filter (0.20 μm). The obtained filtrate was analyzed by high performance liquid chromatography (HPLC, WATERS 600) using an Aminex HPX-87H column (Bio-Rad Lab. Inc.) attached to a refractive index detector. Aq H_2SO_4 (10 mM) at a flow rate of 0.5 mL min^{-1} was run through the column maintained at 323 K. A 20 μL sampling loop was used for injection. A HPLC chromatogram is shown in Figure S1. The conversion, yield and selectivity were calculated using the equations as shown below:

$$\%\text{Conversion} = [\mathit{Amount\ of\ substrate\ used\ (mmol)} - \mathit{Amount\ of\ substrate\ after\ reaction\ (mmol)}] / [\mathit{Amount\ of\ substrate\ used\ (mmol)}] \times 100$$

$$\%\text{Yield} = [\mathit{Number\ of\ carbons\ in\ product} \times \mathit{Amount\ of\ product\ formed\ (mmol)}] / [\mathit{Number\ of\ carbons\ in\ substrate} \times \mathit{Amount\ of\ substrate\ used\ (mmol)}] \times 100$$

$$\%\text{Selectivity} = \frac{\mathit{Yield}}{\mathit{Conversion}} \times 100$$

Recycling experiments were carried out to establish the applicability of the catalyst in the glucose oxidation to FA. After a catalytic run, the reaction mixture was transferred to a centrifugation tube, and the reactor was washed using water to make up volume to 9 mL, followed by centrifugation to decant the supernatant liquid (after a part of the liquid was kept for HPLC analysis). Acetone was added to the left over solid residue and sonicated for a few minutes. The process was repeated three to five times, and the obtained catalyst was dried under vacuum overnight. The dried catalyst was grained and calcined in air at 723 K for 5 h at a ramp rate of 10 K min^{-1}. Thus, obtained catalyst was used for recycle experiments following the method as described above.

An actual concentration of H_2O_2, determined by an iodometric titration method,[43] was found to be 25.4%.

■ RESULTS AND DISCUSSION

Preliminary experiments for the glucose oxidation in water solvent demonstrated that at 363 K the main product was FA with formation of glycolic acid (GA; a C2 carboxylic acid) as a byproduct (Figure 1), which is formed by an oxidative C−C bond cleavage of glucose. At present, we do not consider GA as an intermediate for FA because of its low reactivity (*vide infra*).

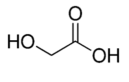
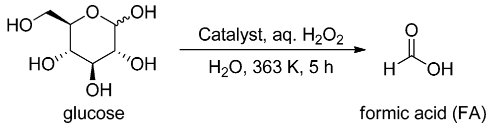


Figure 1. Structure of glycolic acid (GA).

The catalytic activities of various solid catalysts for the glucose oxidation using water as a solvent are shown in Table 1.

Table 1. Oxidation of Glucose over Various Solid Catalysts in Water Solvent.[a]



Entry	Catalyst	Conv/%	FA Yield/%	FA Selectivity/%
1	HT	50.1	23.1	46.1
2	Calcined HT[b]	51.5	29.6	57.5
3	MgO	74.9	37.3	49.9
4	H-ZSM-5	63.8	13.8	21.6
5	H-β zeolite	94.7	25.8	27.2
6	Amberlyst-15	<0.1	-	-
7	γ-Al_2O_3	7.8	-	-
8	SiO_2	13.2	-	-
9	ZrO_2	<0.1	-	-

[a] Reaction conditions: glucose (0.56 mmol), catalyst (0.10 g), water (2.75 mL), 25% H_2O_2 (2.8 mmol), 363 K, 5 h, N_2 atmosphere. [b] Calcined at 723 K in air.

Use of the calcined Mg-Al HT afforded FA with 29.6% yield and 57.5% selectivity at 51.5% glucose conversion (entry 2). Under the same reaction conditions, uncalcined HT and MgO also produced FA; however, the selectivity was less than 50% (entries 1 and 3). Solid acid catalysts such as H-ZSM-5 and H-β zeolites demonstrated lower selectivities for FA (entries 4−5). FA cannot be obtained from the reaction with some other solid acid catalysts, such as Amberyst-15, Al_2O_3, SiO_2 and ZrO_2 (entries 6−9). From these results, the calcined-HT afforded the highest selectivity for FA from glucose, and therefore, we decided to conduct the glucose oxidation using calcined-HTs as catalysts.

Screening of solvent with the calcined-HT catalyst revealed that lower alcohols are suitable for selective synthesis of FA. The FA yields (selectivities) in various solvents at 343 K are as follows: 1-butanol 58% (61%), 1-propanol 53% (62%), ethanol 55% (65%), methanol 54% (65%), water 29% (38%), and DMF 13% (18%). Considering greener aspects and safety of operations, ethanol was chosen as a solvent for further experiments.

In ethanol solvent, the catalytic activities of various catalysts were also examined. For the reaction in ethanol solvent, the glucose oxidation did not occur without catalyst nor aq H_2O_2 (Table 2, entries 1 and 5). During the optimization of the catalytic activity with calcined HT in ethanol, we realized an increase in the FA yields with the increase in amount of aq H_2O_2 and a maximum FA yield was achieve with 5 mmol of aq H_2O_2 (entry 4). A necessity of calcination of the Mg-Al HT was also confirmed since the parent HT failed to produce any FA (entry 2 vs entry 3). Even without calcination, the original Mg-Al HT has basic sites which can work in an aqueous media[41,44,45] (also see Table 1, entry 1) and a change of color of brilliant cresyl blue (pK_a = 11) to a basic color could be observed.[46,47] These basic sites are able to generate OOH^- species from H_2O_2, which oxidizes olefins into the corresponding epoxides.[36,39] In this work, it was observed that parent HT failed to yield FA from glucose in ethanol solvent. These results

Table 2. Effect of Catalyst on FA Selectivity in the Glucose Oxidation Using Aqueous H_2O_2[a]

Entry	Catalyst	Conv/%	Yield/% FA	Yield/% GA	Selectivity to FA/%
1	-	4.8	-	-	-
2	Uncalcined HT	24.7	-	-	-
3	HT[b]	86.4	54.4	3.7	63.0
4[c]	HT[b]	>99	78.1	1.7	78.1
5[d]	HT[b]	24.1	-	15.0	-
6	Uncalcined MgO	36.0	2.9	1.7	8.1
7	MgO[b]	46.6	21.3	2.6	45.8
8	SrO[b]	95.6	29.8	1.3	31.2
9	CaO[b]	50.5	4.2	0.9	8.4
10	Amberlyst-15	43.5	2.1	-	4.8
11	Amberlyst-A26(OH)	30.7	0.3	-	0.9
12	γ-Al_2O_3[b]	25.3	-	-	-
13	Uncalcined H-ZSM-5	58.9	4.9	1.2	8.3
14	H-ZSM-5[b]	13.0	0.8	-	0.9
15	Uncalcined H-β zeolite	61.5	2.4	0.5	3.9
16	H-β zeolite[b]	9.0	-	-	-
17	SiO_2[b]	11.0	-	-	-

[a] Reaction conditions: glucose (0.56 mmol), catalyst (0.10 g), ethanol (2.75 mL), 25% H_2O_2 (2.8 mmol), 343 K, 5 h, N_2 atmosphere. [b] Calcined at 723 K for 5 h in air. [c] 25% H_2O_2 (5 mmol). [d] Without aq H_2O_2.

suggest that the formation of OOH^- species by parent HT and H_2O_2 was inhibited in the presence of ethanol, which is necessary for the FA production[33] (*vide infra*) (entry 2).

Like uncalcined HT catalyst, the uncalcined MgO also demonstrated lower activities for FA formation in ethanol (Table 2, entry 6). Calcination of MgO, SrO and CaO could convert glucose; however, the FA selectivities were low (entries 7–9) compared to that for the calcined-HT due to their strong basicities.[44,45] Large differences between glucose conversions and product yields imply an occurrence of side-reactions.[48] The Amberlyst-15, which has SO_3H moieties as Bronsted acidic sites (H_0: −2.2),[49−52] is not able to produce FA (entry 10). The Amberlyst-A26(OH), known as a strong basic material which contains quaternary ammonium groups,[53] is also incapable of oxidizing glucose to FA (entry 11). Although uncalcined H-ZSM-5 and H-β zeolite catalysts showed activities for FA production in water, the reaction over them failed to progress in ethanol (Table 2, entries 13 and 15). Furthermore, FA cannot be obtained over calcined Al_2O_3, H-ZSM-5, H-β zeolite, and SiO_2 (entries 12, 14, 16, and 17) in ethanol.

The acid catalysts (such as Amberlyst-15 or H-ZSM-5) demonstrated low or no selectivity for FA. In addition, the calcination of solid base catalysts afforded FA under our reaction conditions. Calcination of HT (also see Figure S2) produces Mg-Al mixed oxide with an acid−base bifunctional surface;[42] it is, therefore, suggested that the acid−base pair with a moderate strength on the surface play a pivotal role for the high yield (selectivity) of FA from glucose using aq H_2O_2 in ethanol. The oxygen atoms of glucose molecule might coordinate on the acid sites of calcined HT catalyst, which would react with the OOH^- species generated from H_2O_2 on the neighboring base sites.

The H_2O_2 utilization efficiency is an important assessment in oxidation reactions using H_2O_2 as an oxidant. We calculated the H_2O_2 utilization efficiency based on a titration method, assuming that one mole of glucose produces 6 mol of FA according to the following equation.[29]

$$C_6H_{12}O_6 + 6H_2O_2 \rightarrow 6HCOOH + 6H_2O$$

It should be noted that the H_2O_2 utilization efficiency in this work was almost 100%; 2.5 mmol of H_2O_2 was consumed after the reaction, producing 0.44 mmol of FA. Theoretically, 2.62 mmol of H_2O_2 (=0.44 mmol of FA × 6) should be consumed in this glucose oxidation.[54]

Recyclability of the catalyst is also a key criterion in solid-catalyzed organic reactions.[55] As shown in Figure 2, the calcined Mg-Al HT catalyst is reusable at least twice without losing the high activity and selectivity to FA. The initial kinetics of the reaction for the fresh and spent catalyst were also observed as the similar rate between them (Figure S3). After the reaction, the mixed Mg-Al oxide structure of the calcined HT could be transformed to the layered HT structure with water (memory effect[35]) and lose its activity. In recycling experiments, therefore, the used HT catalyst was washed with acetone and dried at room temperature under a vacuum, followed by calcination at 773 K prior to the further reactions. Also, the X-ray diffraction (XRD) patterns of the catalyst before the catalytic run (calcined hydrotalcite) can be observed again after the calcination of the used catalyst (see Figure S2).

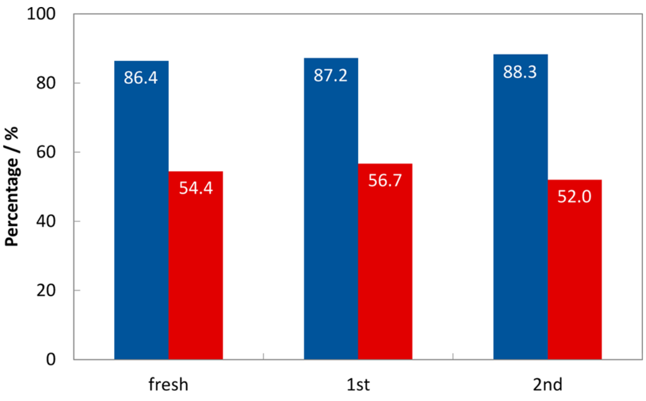


Figure 2. Reusability of calcined HT catalyst for the oxidation of glucose using aq H_2O_2. Blue and red bars are the conversion of glucose and the yield of FA, respectively. Reaction conditions: glucose (0.56 mmol), calcined Mg-Al HT (0.10 g), ethanol (2.75 mL), 25% H_2O_2 (2.8 mmol), 343 K, 5 h, N_2 atmosphere. The numbers indicate the conversion and yield of glucose and FA, respectively.

Viability of this catalytic system has been evaluated for the oxidation of various monosaccharides including pentoses into FA in the presence of aq H_2O_2 (5 mmol). As shown in Figure 3, we successfully found that various monosaccharides, including fructose, galactose, xylose, arabinose and lyxose, could be transformed to FA in good yields (>70%) with 100% saccharide conversion. In the case of fructose, however, the oxidation was not selective; GA was also formed considerably. A keto group at the second carbon in fructose may facilitate a cleavage of the bond between the second and third carbons, which resulted in GA formation (see Scheme S1 for the GA formation mechanism).

According to Isbel and Naves,[33] it was expected that oxidation of aldohexose would begin with the addition of OOH^- species to the aldehydic carbon atom of the acyclic form of the aldohexose (Scheme S2), followed by decomposition to the next lower aldohexose and formic acid (Scheme 2).

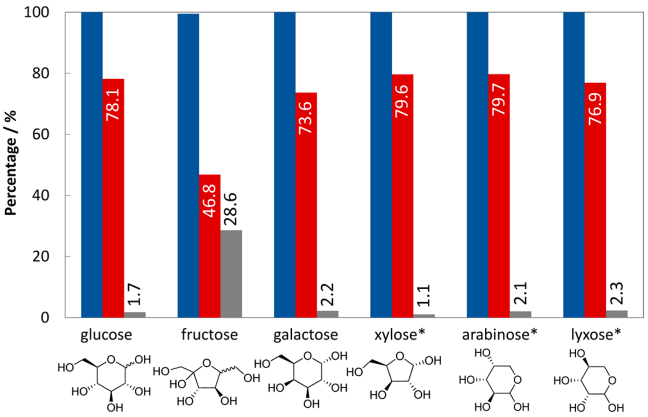
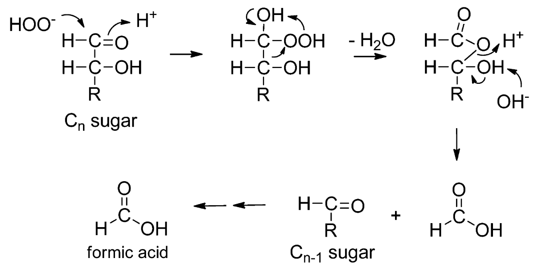


Figure 3. Oxidation of various monosaccharides over calcined-HT catalyst using aq H_2O_2: blue bar (conversion), red bar (FA yield), and gray bar (yield of GA). Reaction conditions: saccharide (0.56 mmol), calcined Mg-Al HT (0.10 g), ethanol (2.75 mL), 25% H_2O_2 (5 mmol), 343 K, 5 h, N_2 atmosphere. *Substrate (0.67 mmol). The conversion was >99% in all cases. The numbers indicate the corresponding yields of FA and GA.

Scheme 2. Oxidation of Acyclic Form of Aldohexoses by Hydroperoxide Anion into Formic Acid (FA)



CONCLUSION

In conclusion, we found that FA can be produced from various hexoses and pentoses using calcined Mg-Al hydrotalcite catalyst in the presence of 25% aqueous H_2O_2 in ethanol solvent with an excellent H_2O_2 utilization efficiency. The used hydrotalcite catalyst can be easily separated from the reaction mixture and can be reused at least twice.

ASSOCIATED CONTENT

Ⓢ Supporting Information

HPLC chromatogram, XRD, acyclic forms of saccharides, and proposed reaction pathway. 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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REFERENCES

(1) Mori, K.; Dojo, M.; Yamashita, H. *ACS Catal.* **2013**, *3*, 1114−1119.
(2) Boddien, A.; Mellmann, D.; Gärtner, F.; Jackstell, R.; Junge, H.; Dyson, P. J.; Laurenczy, G.; Ludwig, R.; Beller, M. *Science* **2011**, *333*, 1733−1736.
(3) Huang, Y.; Zhou, X.; Yin, M.; Li, C.; Xing, W. *Chem. Mater.* **2010**, *22*, 5122−5128.
(4) Yasaka, Y.; Wakai, C.; Matsubayashi, N.; Nakahara, M. *J. Phys. Chem. A* **2010**, *114*, 3510−3515.
(5) Fellay, C.; Dyson, P. J.; Laurenczy, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 3966−3968.
(6) Loges, B.; Boddien, A.; Junge, H.; Beller, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3962−3965.
(7) Farkas, E.; Sunman, C. J. *J. Org. Chem.* **1985**, *50*, 1110−1112.
(8) Lukasiewicz, A. *Tetrahedron* **1963**, *19*, 1789−1799.
(9) Tuteja, J.; Choudhary, H.; Nishimura, S.; Ebitani, K. *ChemSusChem* **2014**, *7*, 96−100.
(10) Son, P. A.; Nishimura, S.; Ebitani, K. *RSC Adv.* **2014**, *4*, 10525−10530.
(11) Broggi, J.; Jurcil, V.; Songis, O.; Poater, A.; Cavallo, L.; Slawin, A. M. Z.; Cazin, C. S. J. *J. Am. Chem. Soc.* **2013**, *135*, 4588−4591.
(12) Wienhofer, G.; Sorribes, I.; Boddien, A.; Westerhaus, F.; Junge, K.; Junge, H.; Llusar, R.; Beller, M. *J. Am. Chem. Soc.* **2011**, *133*, 12875−12879.
(13) Choudhary, H.; Nishimura, S.; Ebitani, K., submitted for publication, 2015.
(14) Ordal, E. J.; Halvorson, H. O. *J. Bacteriol.* **1939**, *38*, 199−220.
(15) Reutemann, W.; Kieczka, H. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2005.
(16) Hull, J. F.; Himeda, Y.; Wang, W. H.; Hashiguchi, B.; Periana, R.; Szalda, D. J.; Muckerman, J. T.; Fujita, E. *Nat. Chem.* **2012**, *4*, 383−388.
(17) Wesselbaum, S.; Hintermair, U.; Leitner, W. *Angew. Chem., Int. Ed.* **2012**, *51*, 8585−8588.
(18) Zhang, Z.; Hu, S.; Song, J.; Li, W.; Yang, G.; Han, B. *ChemSusChem* **2009**, *2*, 234−238.
(19) Zhang, Z.; Xie, Y.; Li, W.; Hu, S.; Song, J.; Jiang, T.; Han, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 1127−1129.
(20) Ohlin, C. A.; Laurenczy, G. *High Pressure Res.* **2003**, *23*, 239−242.
(21) Bui, L.; Luo, H.; Gunther, W. R.; Roman-Leshkov, Y. *Angew. Chem., Int. Ed.* **2013**, *52*, 8022−8025.
(22) Bui, P.; Cecilia, J. A.; Oyama, S. T.; Takagaki, A.; Infantes-Molina, A.; Zhao, H.; Li, D.; Rodriguez-Castellon, E.; Lopez, A. J. *J. Catal.* **2012**, *294*, 184−198.
(23) Nakajima, K.; Baba, Y.; Noma, R.; Kitano, M.; Kondo, J. N.; Hayashi, S.; Hara, M. *J. Am. Chem. Soc.* **2011**, *133*, 4224−4227.
(24) Nakagawa, Y.; Shinmi, Y.; Koso, S.; Tomishige, K. *J. Catal.* **2010**, *272*, 191−194.
(25) Huber, G. W.; Iborra, S.; Corma, A. *Chem. Rev.* **2006**, *106*, 4044−4098.
(26) Fukuoka, A.; Dhepe, P. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 5161−5163.
(27) Choudhary, H.; Nishimura, S.; Ebitani, K. *Appl. Catal. B: Environ.* **2015**, *162*, 1−10.
(28) Ahlkvist, J.; Ajakumar, S.; Larsson, W.; Mikkola, J.-P. *Appl. Catal. A: Gen.* **2013**, *454*, 21−29.
(29) Jin, F.; Enomoto, H. *Energy Environ. Sci.* **2011**, *4*, 382−397.
(30) Wölfel, R.; Taccardi, N.; Bösmann, A.; Wasserscheid, P. *Green Chem.* **2011**, *13*, 2759−2763.
(31) Jin, F.; Yun, J.; Li, G.; Kishita, A.; Tohjo, K.; Enomoto, H. *Green Chem.* **2008**, *10*, 612−615.
(32) Isbell, H. S. *Carbohydr. Res.* **1976**, *49*, C1−C4.
(33) Isbell, H. S.; Naves, R. G. *Carbohydr. Res.* **1974**, *36*, C1−C4.
(34) Isbell, H. S.; Frush, H. L. *Carbohydr. Res.* **1973**, *28*, 295−301.
(35) Miyata, S. *Clays Clay Miner.* **1980**, *28*, 50−56.

(36) Honma, T.; Nakajo, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Tetrahedron Lett.* **2002**, *43*, 6229−6232.

(37) Fraile, J. M.; García, J. I.; Moyoral, J. A.; Sebti, S.; Tahir, T. *Green Chem.* **2001**, *3*, 271−274.

(38) Aramendía, M. A.; Borau, V.; Jiménez, C.; Luque, J. M.; Marinas, N. M.; Ruiz, J. R.; Urbano, F. J. *Appl. Catal. A: Gen.* **2001**, *216*, 257−265.

(39) Yamaguchi, K.; Ebitani, K.; Kaneda, K. *J. Org. Chem.* **1999**, *64*, 2966−2968.

(40) Cativiera, C.; Figueras, F.; Fraile, J. M.; García, J. I.; Moyoral, J. A. *Tetrahedron Lett.* **1995**, *36*, 4125−4128.

(41) Nishimura, S.; Takagaki, A.; Ebitani, K. *Green Chem.* **2013**, *15*, 2026−2042 (review).

(42) Yamaguchi, K.; Ebitani, K.; Yoshida, T.; Yoshida, H.; Kaneda, K. *J. Am. Chem. Soc.* **1999**, *121*, 4526−4527.

(43) *Determination of Hydrogen Peroxide Concentration*; Technical Data Sheet; Solvay Chemicals, Inc.: USA, 2004.

(44) Ono, Y.; Hattori, H. In *Solid Base Catalysis*; Castleman, A. W. Jr., Toennis, J. T., Yamanouchi, K., Zinth, W., Eds.; Springer series in Chemical Physics 101; Tokyo Institute Technology Press-Springer: Tokyo-Berlin, 2010.

(45) Tanabe, K.; Misono, M.; Ono, Y.; Hattori, H. In *New Solid Acids and Bases. Their Catalytic Properties*; Delmon, B., Yates, J. T., Eds.; Studies in Surface Science and Catalysis 51; Kodansha-Elsevier: Tokyo-Amsterdam, 1989.

(46) Son, P. A.; Nishimura, S.; Ebitani, K. *React. Kinet. Mech. Catal.* **2014**, *111*, 183−197.

(47) Gupta, N. K.; Nishimura, S.; Takagaki, A.; Ebitani, K. *Green Chem.* **2011**, *13*, 824−827.

(48) At this time, however, we were unable to verify the products by side-reactions.

(49) Farcasiu, D.; Ghenciu, A.; Marino, G.; Rose, K. D. *J. Am. Chem. Soc.* **1997**, *119*, 11826−11831.

(50) Choudhary, H.; Nishimura, S.; Ebitani, K. *Appl. Catal. A: Gen.* **2013**, *458*, 55−62.

(51) Son, P. A.; Nishimura, S.; Ebitani, K. *React. Kinet. Mech. Catal.* **2012**, *106*, 185−192.

(52) Choudhary, H.; Nishimura, S.; Ebitani, K. *Chem. Lett.* **2012**, *41*, 409−411.

(53) http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_08d3/0901b803808d3097.pdf?filepath=liquidseps/pdfs/noreg/177-03098.pdf&fromPage=GetDoc (Latest Retrieved on 12th December, 2014).

(54) The high utilization efficiency of H_2O_2 indicates that only a minimal amount of H_2O_2 was left after the catalytic oxidation of glucose. Thereby, the probability of the chemical reaction between formed FA and left H_2O_2 is very low to form side products such as performic acid. Additionally, in a control experiment 2 mmol of FA was stirred with 2.8 mmol of H_2O_2 at 343 K for 5 h to observe only 11% conversion of FA. These results rule out the possibility of formation of performic acid under our reaction conditions.

(55) Sheldon, R. A.; Wallau, M.; Arends, I. W. C. E.; Schuchardt, U. *Acc. Chem. Res.* **1998**, *31*, 485−493.

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