CATALYTIC HYDROGENATION AND OXIDATION OF BIOMASS-DERIVED LEVULINIC ACID

Yan Gong, Lu Lin,* and Zhipei Yan

Levulinic acid (LA), 4-oxo-pentanoic acid, is a new platform chemical with various potential uses. In this paper, catalytic hydrogenation and oxidation of levulinic acid were studied. It was shown from experiments that levulinic acid can be hydrogenated to γ-valerolactone (GVL) over transition metal catalysts and oxidative-decarboxylated to 2-butanone (methyl-ethyl-ketone, MEK) and methyl-vinyl-ketone (MVK) by cupric oxide (CuO), cupric oxide/cerium oxide (CuO/CeO_2), cupric oxide/ alumina (CuO/Al_2O_3), and silver(I)/ peroxydisulfate ($Ag(I)/S_2O_8^{2-}$).

Keywords: LA; Hydrogenation; Oxidation; GVL; MEK; MVK

Contact information: Department of Resources Science and Engineering, State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China, 510640;
**Corresponding author: lclulin@scut.edu.cn (Lin)*

INTRODUCTION

In recent decades the demand for natural resources has been increasing at an amazing rate. However, fossil fuel sources are on the course of rapid depletion, while environmental pollution and severe climate impacts are gradually becoming serious due to over-exploitation and over-use of fossil fuels. Thus, renewable chemical and energy resources need to be urgently developed and the utilization of biomass of energy, chemicals, and materials has received a good deal of attention.

Cellulose, the most abundant renewable polymer available, is produced by nature at an annual rate of 10^{11} to 10^{12} tons (Hon 1994). It can be efficiently converted to monomeric sugars by hydrolytic processes and can play an important role to meet future energy needs.

Levulinic acid (LA), a short chain fatty acid, is another product of acidic hydrolysis of cellulose and also one of the extracts from black liquor of the paper-making process (He 1999). It is used in many fields such as textile dyeing, antifreezing, animal fodders, coating materials, solvents, food flavoring agents, pharmaceutical compounds and resin, etc. (Chang et al. 2007 ; Cha et al. 2002; Fang et al. 2002). The reactivity of levulinic acid lies in its molecular structure that contains a carbonyl group and a carboxyl group.

In this paper, study of catalytic hydrogenation and oxidation of levulinic aicd was conducted for its new prospective applications as fuels and high-value chemicals in the future (Scheme 1).

EXPERIMENTAL

Materials

Levulinic acid, Pd/C, Raney Ni and Urushibara Ni (U–Ni–A(S)) and Ruthenium/ C (Ru/C) was purchased from the Shanghai Jingchun Chemical Company. The metal oxides, silver nitrate, and potassium peroxydisulfate were obtained from Kermal Company (Tianjin, AR) or Sinopharm Company (Beijing, AR) and used without further purifications.

Procedure of Catalytic Hydrogenation of LA by Metal Catalysts

The experiments of LA hydrogenation at elevated pressure were performed in a 1000 mL steel autoclave made by Büchi of Switzerland. A 300 mL portion of a 5wt % solution of LA in methanol with catalyst was pumped into the autoclave. The system was flushed with hydrogen.

Procedure of LA Deacrboxylation by Metal Oxides

The experiments were carried out in a 4576-HP / HT Pressure Reactor (200 mL, PARR INSTRUMENT). Levulinic acid (0.01 mol) with metal oxide was added into KH_2PO_4-NaOH (0.2 mol/L) solution, and the initial pH was adjusted with NaOH (0.2 mol/L). The total volume was kept at 60 mL.

Procedure of LA oxidation by CuO/CeO_2 and CuO/ Al_2O_3

The experiments were performed in a PARR-5050 Pressure Reactor (100mL, Parr Instruments Company). Reaction solutions were obtained by adding levulinic acid (0.01mol) into KH_2PO_4 (0.2mol/L) solution, then CuO/CeO_2 or CuO/ Al_2O_3 was added into the prepared reaction solutions. The total volume was 60mL.

Procedure of LA oxidation by metal ion/peroxydisulfate

Batch experiments were performed in a DF-101S oil bath (Yu Hua instrument), and a PARR-5050 Pressure Reactor (100 mL, Parr Instruments Company). Reaction solutions were obtained by adding levulinic acid (0.01 mol) into KH_2PO_4-NaOH (0.2 mol/L) solution, then silver nitrate (0.01 mol) and potassium peroxdisulfate and silver nitrate were sequentially added into the prepared reaction solutions. The total volume was 60 mL.

Gas Chromatography Detection for GVL

Samples taken during LA hydrogenation were analyzed with a GC using an Agilent 6820 (G1176A) gas chromatograph equipped with an HP Innowax polyethylene glycol capillary column with dimensions of 30 m × 250 µm i.d. × 0.25 µm film and a flame ionization detector (FID) operating at 250 °C. The carrier gas was helium with a flow rate of 1.0 mL/min. The following temperature program was used in the analysis: 60°C (1 min) — 10°C/min — 230°C (5min). The sample analysis was confirmed with a gas chromatograph Agilent 6890 5975 GC - MS instrument, equipped with the HP Innowax polyethylene glycol capillary column with the same analysis conditions. The injector temperature was 250°C, and the mass spectrometer used an electron impact (EI) ionization mode with 70 eV of electron energy.

Head Space – Gas Chromatography Detection for MEK and MVK

Head space (HSS 86.50) - gas chromatography (QP2010, Shi-madzu Japan) **(**HS-GC) was used extensively in the separation and identification of mixtures of volatile compounds. The volatile products of LA decarboxylation were analyzed by HS-GC using a DB-5 column (30m× 0.25 mm i.d. × 0.25μm film) at a column temperature of 200°C, a flow rate of 4.7mL/min, and with a flame ionization detector at the temperature of 250°C. The analysis was performed at 60°C for 5 min. The component concentrations were calculated by the area normalization method. The sample vials were shaken for 20 min at the temperature of 75°C. The temperatures of sampling probe and tube were 85°C and 95°C, respectively. Automatic sampling was employed.

Ion Chromatography Detection for LA

Ion chromatography (ICS-3000, DIONEX USA) was used for the analysis of levulinic acid in the aqueous phase to figure out the conversion of levulinic acid. Liquid reactant after the reactions was filtrated and diluted before testing. The analysis was conducted in an anion-exchange column (AS11-HC) with 2mol/L NaOH leacheate in a conductivity cell at 35°C. The flow rate was 1.0 mL/min, and the sample size was 50μL. The calibration was performed using aqueous solutions.

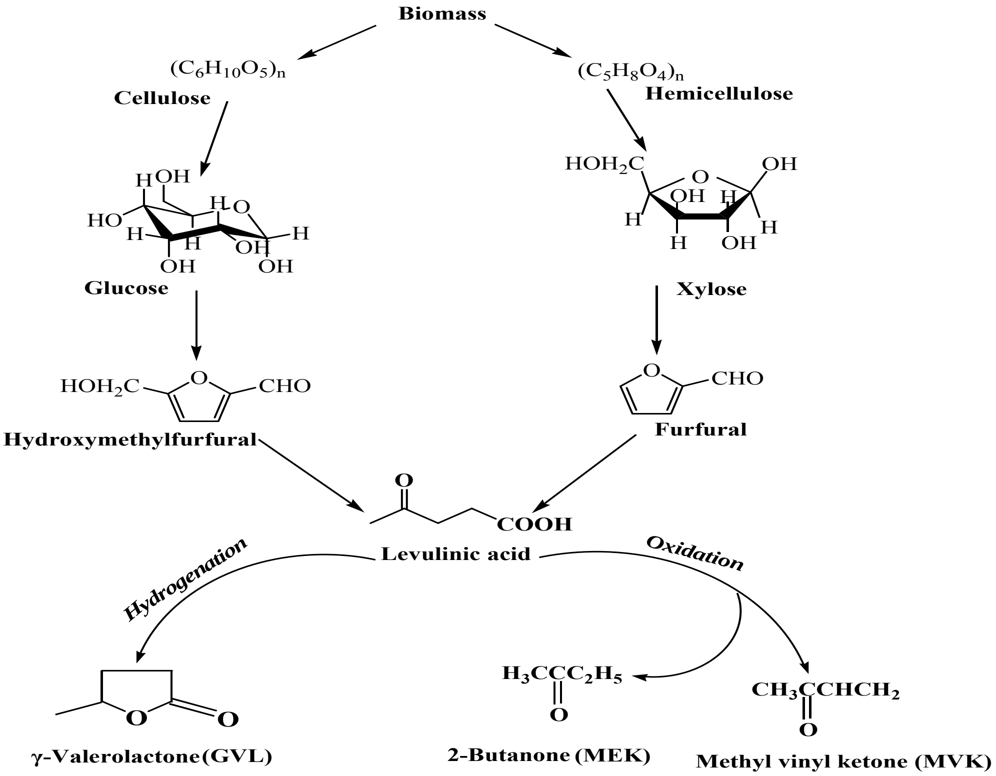
RESULTS AND DISCUSSION

LA Hydrogenation

GVL is a naturally occurring chemical in fruits and a frequently used food additive. It is renewable and it also has potential use as a monomer for polyester production. It exhibits the most important characteristics of an ideal sustainable liquid, since it is convertible to both energy and carbon-based consumer products.

LA hydrogenation has been extensively investigated for the transformation of LA to GVL over metallic catalysts including platinum oxide (Schuette et al. 1930), Raney nickel (Christian et al. 1947), rheniumheptoxide (Broadbent et al. 1959), ruthenium and rhodium complexes (Joo et al. 1984), rutheniumiodocarbonyl complexes (Braca et al. 1991), and ruthenium triphenyl phosphine complexes (Osakada et al. 1982). In this experiment, Ru/C was firstly employed to catalyze conversion of levulinic aicd to GVL. Under the following conditions: 130 °C of the temperature, 1.2 Mpa of hydrogen pressure, 160 min of reaction time with the dosage of 5% catalyst (based on the mass fraction of LA), and 95% methanol as solvent, GVL is formed with the highest selectivity and LA conversion was also the highest with Ru/C as catalyst, compared with those in the presence of other catalysts, such as Pd/C, Raney Ni, and U–Ni–A(S), as shown in Table 1. Solvents played an important role for LA conversion to GVL. When absolute methanol was used as solvent, the LA conversion and GVL selectivity reached 92.90% and 99.03%, respectively; nevertheless, normal butanol, benzaldehyde, DMSO, and 1,4-dioxane did not work (Table 2).

The hydrogenation mechanism of LA has been proposed to involve the breakage of the double bond (C=O) in the carbonyl group, followed by addition of two H atoms, and in this process γ-hydroxyvaleric acid is formed. The hydroxyl group can interact with the carboxyl group in γ-hydroxyvaleric acid, such that one molecule of H_2O is lost by heat treatment.



Scheme 1. Proposed pathway of hydrogenation and oxidation of levulinic acid

Table 1. Effects of Various Catalysts on LA Hydrogenation

Catalysts	LA Conversion /%	GVL Selectivity /%
Ru/C	92.36	98.83
Pd/C	17.89	40.22
Raney Ni	18.88	31.93
U–Ni–A(S)	46.58	8.07

Table 2. Effect of Varies Solvents on LA Hydrogenation

Solvents	LA Conversion /%	GVL Selectivity /%
Absolute methanol	92.90	99.03
Mormal butanol	0	0
Benzaldehyde	0	0
DMSO	0	0
1，4–dioxane	4.32	0

LA Oxidation

2-butanone (MEK) is an essential component of the distillate (alcohol oil) derived from the destructive distillation of wood. In industry, it is the product from the hydrogention of butanol and the water oxidation of butene. It can also be produced from methyl formate, which reacts with ethylene and carbon monoxide in the presence of a rhodium catalyst with an ionic iodide as promotor, as reported by Mathe et al (1991). Butanone is usually used as a solvent in organic synthesis. It can be converted through Baeyer-Villiger oxidation to ethyl acetate (Williamd et al. 1955), which is further reduced to ethanol. Besides, it can also be hydrogenated to butanol (Lou et al. 2010; Gao et al. 2007), which is a cleaner and superior fuel to ethanol with octane numbers 113 and 94 as compared with that of 111 and 94 of ethanol (Qureshi et al. 2008). Thus, decarboxylation of levulinic acid to produce butanone might be one of the key conversion steps from biomass-derived carbohydrates to versatile fuels. Methyl-vinyl-ketone (MVK) is a degradation product of isoprene (Trapp et al. 2001; Iannone et al. 2009) or the dehydration product of 4-hyfroxy-2-butanone, which is obtained from the condensation reaction of acetone and formaldehyde. It can react with O_3 in the atmosphere, leading to the OH radical (Aschmann et al. 1996) and can be involved in the aza-Morita–Baylis–Hillman reactions (aza-MBH) of imines as a Michael acceptor (Gao et al. 2006). Moreover, it is an alkylating agent and the intermediate of synthesis of steroids and vitamin A.

LA Reacting with Metal Oxides

Decarboxylation of organic molecules refers to the removal of a carboxyl group from its chemical structure and its further replacement by a hydrogen atom. Oxidative decarboxylation of saturated and aryl-substituted carboxylic acids and their derivatives has been extensively studied over various oxidants involving supported manganese(Ш) porphyrin (Mirkhani et al. 2003), manganese(III) Schiff base complexes (Mirkhani et al. 2004), active hydroxyl radicals (•OH) (Guitton et al. 1998), peroxyl radicals (Lamrini et al. 1998), and high-valent metal ions (Trahanovsky et al. 1974), etc. Thermal decarboxylations of iron hydroxide cetylsulfonyl acetate (Zhang et al. 2008), tryptophan (Martins et al. 2008), and perfluoropolyether salts (Marchionni et al. 2003) have received a good deal of attention. Moreover, photolytic decarboxylation (PD) plays an important role in several areas of study. It has been commonly used to prepare radical intermediates and organic compounds and also applied in pharmaceuticals and agriculture. Farhadi et al.

(2006) have found that α-arylcarboxylic acids can be converted into corresponding aldehydes and ketones selectively catalyzed by HgF_2 under irradiation condition in the presence of oxygen gas. Up to date, efficient, and clean methods for LA decarboxylation have not been previously investigated. Chum et al. (1983) explored the photo-electrochemical reaction of levulinic acid on undoped platinized n-TiO_2 powders, leading to generation of MEK, propionic acid, acetic acid, acetone, and acetaldehyde as major products. Even under the most compatible conditions designed, the yield of MEK was not satisfactory.

In this study, decarboxylation of LA was firstly conducted with calcium oxide (CaO) for 3h in neutral KH_2PO_4-NaOH solution at 300°C. The MEK yield and LA conversion reached 15.7% and 81.5%, respectively, which was not satisfactory. As a result, decarboxylation of LA was examined by using other metal oxides under the same conditions. The results are summarized in Table 3. As seen in Table 3, when

Table 3. Decarboxylation of LA Catalyzed by Different Metal Oxides

Metal oxide	MEK Yield /%	Acetone Yield /%	LA Conversion /%
—	12.09	2.04	40.11
CaO	15.72	2.07	81.48
MgO	18.80	2.27	73.74
ZnO	26.80	2.89	78.26
CuO	57.23	17.85	99.06
Al_2O_3	14.47	1.62	45.93
Fe_2O_3	17.43	2.18	53.96
TiO_2	13.32	1.44	74.45
ZrO_2	12.55	1.65	53.29

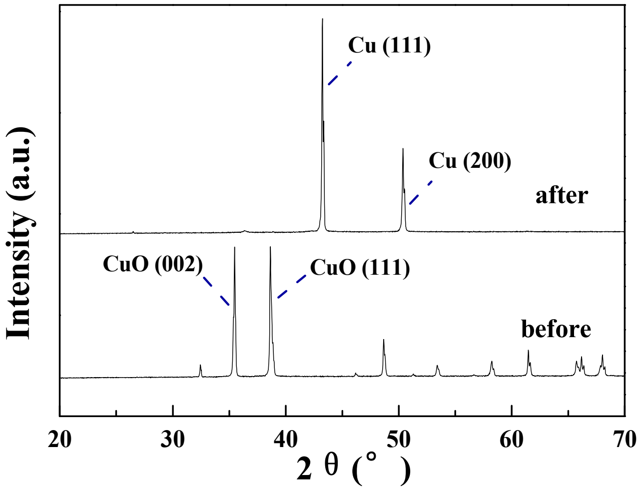


Fig. 1. X-Ray diffraction spectra of CuO and the precipitate of elemental Cu generated during the reaction of decarboxylation of LA

CuO was present, LA can be decarboxylated to MEK (57.23% yield of MEK detected by GC; 99% of conversion rate detected by ion chromatography). As for ZnO as catalyst, the rate of MEK ranked second, 26.8%. The rest of the metal oxides used in the experiment were less effective for decarboxylation of LA to MEK; yields of MEK were lower than 20%. CuO was shown to be particularly active and selective for LA decarboxylation. Surface chemistry of CuO was characterized by XRD before and after reaction, as shown in Fig. 1. The XRD spectrum of CuO showed two strong peaks at 2θ = 35.5° and 38.6°, corresponding to the (002) and (111) planes of monoclinic CuO, respectively, acclaimed by Hoa et al. (2010). The XRD spectrum of precipitate after the reactions showed that the peaks corresponding to CuO disappeared and peaks corres-ponding to Cu [2θ = 43.3°(111) and 50.4°(200)] appeared instead. This result indicated that CuO was completely reduced to elemental form (Cu) at 300°C during the reaction of LA decarboxylation.

Then, the thermal desorption of hydrogen (H_2) adsorbed on CuO was investigated, and the TPR profile in Fig. 2 showed that two reduction peaks were present, the first one at about 300°C and the second one at about 450°C, indicating the existence of two CuO species (isolated Cu^{2+} and bulk CuO). The reduction of bulk CuO took place in a one-step mechanism, that is, CuO was directly converted to Cu; according to the configuration of extra-nuclear electron Cu^{2+} and Cu^{+}, Cu^{+} was more stable than Cu^{2+}; thus the reduction of isolated Cu^{2+} occurred by a two-step mechanism in which Cu^{2+} was first reduced to Cu^{+} at 300°C and further reduced to Cu at about 450°C. But in this reaction, Cu^{+} seemed rather active and was reduced to Cu at 300°C. In the remaining experiments, the effect of CuO dosage, reaction time, and initial pH values in the presence of CuO were studied. Under the optimum reaction conditions (pH: 3.2; time: 2h; CuO dosage: 69%), MEK yield was 67%.

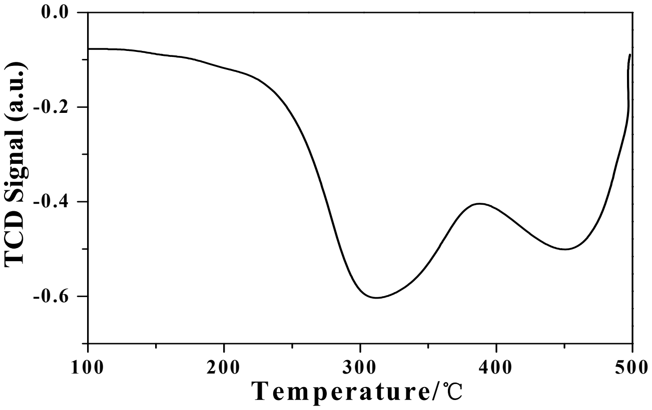


Fig. 2. Temperature programmed reduction profile of CuO

LA decarboxylation by CuO was assigned as an oxidation reaction. It is proposed that the initial attack of Cu(II) is initiated by the molecule of LA, producing $CH_3COCH_2CH_2CO_2\bullet$. Then, the copper becomes reduced to the elemental form. $CH_3COCH_2CH_2CO_2\bullet$ followed by a subsequent dissociation of group of CO_2 to form $CH_3COCH_2CH_2\bullet$ and CO_2. On the basis of results from HS-GC-MS, $CH_3COCH_2CH_2\bullet$ should then be scavenged by a hydrogen-donating species to produce MEK.

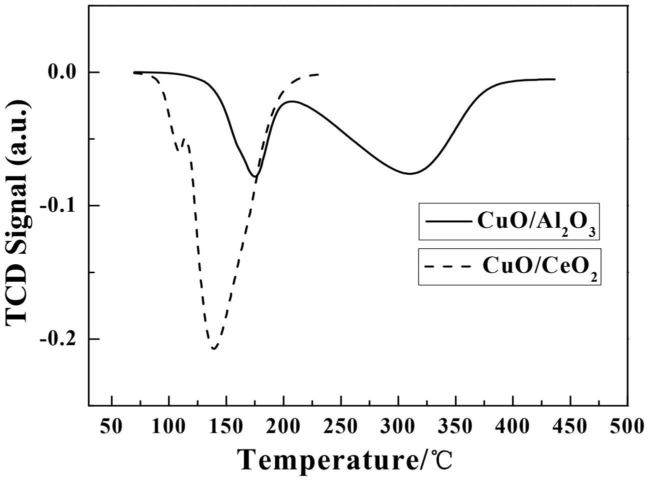


Fig. 3. Temperature programmed reduction profiles of CuO/CeO_2 (15%) and CuO/ Al_2O_3 (15%)

LA Reacting with CuO/CeO_2 and CuO/ Al_2O_3

CuO can effectively oxidize LA to undergo decarboxylation reaction to produce MEK. However, the reaction temperature of 300°C seemed extremely high. The search for mild reactive conditions together with high catalytic efficiency is imperative for the future potential industrial applications and meaningful in organic synthesis. It was reported that with CuO-modified catalysts such as CuO/CeO_2 (Luo et al. 1997), CuO/Al_2O_3 (Luo et al. 2005), etc., the reaction could be achieved at lower temperature. Thus, CuO/CeO_2 (15%) and CuO/Al_2O_3 (15%) were prepared, and the H_2-TPR measurements of these two catalysts were conducted (Fig. 3). The presence of two TPR peaks in Fig. 3 indicated that there were two reducible copper species in both profiles; a peak at low-temperature due to the reduction of highly dispersed CuO species and another peak at high-temperature peak due to the reduction of bulk CuO were evident. The temperatures for TPR peaks of CuO/CeO_2 were about 110°C and 140°C, and temperatures for TPR peaks of CuO/Al_2O_3 were about 175°C and 310°C, much lower than that of pure CuO. The experiments of decarboxylation of LA by CuO/CeO_2 and CuO/Al_2O_3 were separately carried out in KH_2PO_4 solution (pH 3.2) at 175°C. In these experiments, methyl-vinyl-ketone(MVK) was produced as a main gaseous product (about 18% by CuO/CeO_2 and 10% by CuO/Al_2O_3, detected by HS-GC-MS). The by-products such as acetone, ethyl acetate and 2,3-butanedione were also detected. In the XRD spectra (Fig. 4) of the CuO/CeO_2, CuO/Al_2O_3, and filtered precipitates after reaction, it was found that peaks corresponding to CeO_2 and Al_2O_3 were still present after reaction, but the intensity of the peaks decreased evidently. Meanwhile, the peaks corresponding to CuO disappeared. These results indicated that CuO in CuO/CeO_2 and CuO/Al_2O_3 could be reduced at 175°C. CeO_2 could promote the hydrogen reduction activity of copper, thus, CuO/CeO_2 showed a different catalytic behavior with respect to pure CuO, which may oxidize $CH_3COCH_2CH_2$• to MVK. Al_2O_3 could also promote the oxidative decarboxylation of LA by CuO existing in the complex of CuO/Al_2O_3.

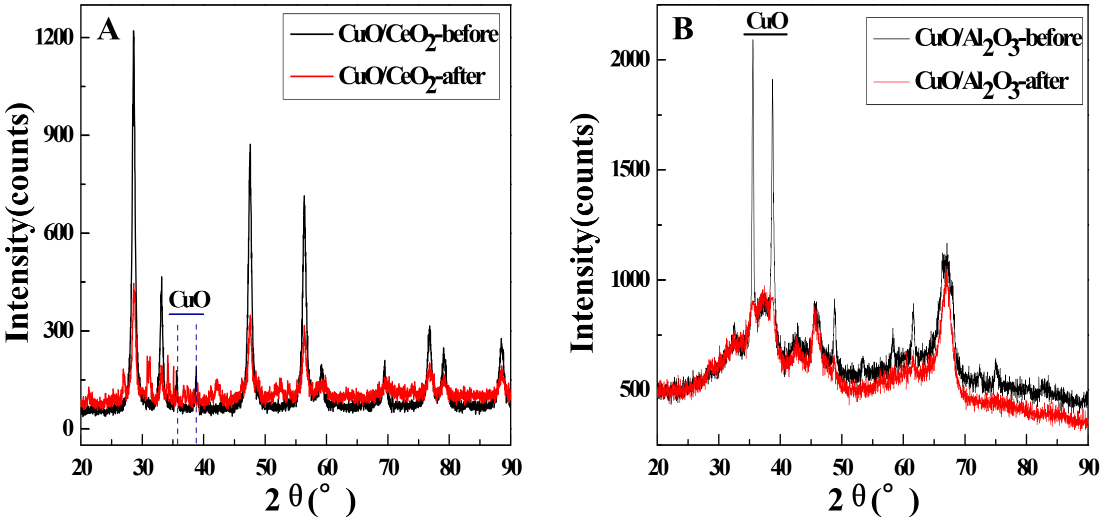


Fig. 4. The X-Ray Diffraction Spectrua of CuO/CeO_2 (A) and CuO/Al_2O_3 (B)

LA Reacting with Metal Ion/ Peroxydisulfate

The readily available peroxydisulfate anion, $S_2O_8^{2-}$, is an excellent and versatile oxidant in a variety of reactions happening between organic and inorganic compounds. It has been previously demonstrated to be effective to oxidize both aromatic rings and aryl acids with (Jonsson et al. 1979; Walling et al. 1978; O'Neill et al. 1975) or without (Eberhardt 1981) various metal catalysts. In the course of this study, oxidative decarboxylation of LA by peroxydisulfate with metal ions such as Ag(I) or Cu(I) was conducted (Table 4). Batch experiments were performed in a DF-101S oil bath (Yu Hua instrument) at the temperature of 100°C for 0.5 h. The results showed that $Ag(I)/S_2O_8^{2-}$ was the most effective agent for LA deacrboxylation to butanone. Then, based on Ag(I) as catalyst, the effects of buffer solution, initial pH value, dosages of $Ag(I)/S_2O_8^{2-}$, reaction time, and temperature exerted on decarboxylation of LA were examined. The results showed that the solution of $NaOH\text{-}KH_2PO_4$ was comparatively suitable for LA decarboxylation, because MEK was the single product in the gas phase; and under an optimum condition (160 °C of temperature, 5.0 of pH value, and 0.5h of reaction time), about 71% rate of LA conversion in $NaOH\text{-}KH_2PO_4$ solutions with an initial concentration of 0.01 mol/L was achieved, the molar yield of butanone reached 44.2%. LA was oxidized by peroxydisulfate either with or without Ag(I), and the rates of LA conversion and MEK yield were similar [69.3% and 35.9% without Ag(I), 69% and 36.2% with Ag(I)]. Moreover, Ag(I) without peroxydisulfate could react with LA to form MEK (LA conversion 12.9%, MEK yield 1.2%).

A mechanism to account for oxidative decarboxylation of LA by Ag(II), produced by peroxydisulfate oxidation of Ag(I), is proposed in Eqs. 1 through 5. The oxidation of Ag(I) by persulfate (Eq.1) followed in quick succession by a second oxidation by the sulfate ion radical (Eq. 2) is in accordance with the kinetic study of the persulfate oxidation demonstrated by Miller (1968).

$$\mathrm{Ag(I)} + \mathrm{S_2O_8^{2-}} \longrightarrow \mathrm{Ag(II)} + \mathrm{SO_4^{-}\bullet} + \mathrm{SO_4^{2-}} \quad (1)$$

$$\mathrm{Ag(I)} + \mathrm{SO_4^{-}\bullet} \longrightarrow \mathrm{Ag(II)} + \mathrm{SO_4^{2-}} \quad (2)$$

$$\mathrm{Ag(II)} + \mathrm{CH_3COCH_2CH_2COOH} \longrightarrow \mathrm{Ag(I)} + \mathrm{CH_3COCH_2CH_2COO\bullet} + \mathrm{H^+} \quad (3)$$

$$\mathrm{CH_3COCH_2CH_2COO\bullet} \longrightarrow \mathrm{CH_3COCH_2CH_2\bullet} + \mathrm{CO_2} \quad (4)$$

$$\mathrm{CH_3COCH_2CH_2\bullet} + \mathrm{H\text{-}Solv} \longrightarrow \mathrm{CH_3COCH_2CH_3} + \mathrm{\bullet Solv} \quad (5)$$

Direct and facile oxidation of LA by Ag(II) in a fast follow-up step could generate a radical $CH_3COCH_2CH_2CO_2\bullet$, which is subsequently fragmented to $CH_3COCH_2CH_2\bullet$ and CO_2. MEK is derived by oxidation of the $CH_3COCH_2CH_2\bullet$ catalyzed by silver species as well as by hydrogen transfer to the solvent (Eqs. 1-5). It was said that the activation process for Ag(I)-catalyzed oxidative decarboxylation by persulfate is mainly associated with the formation of Ag(II) species (Anderson et al. 1970), but it appeared that that yield of butanone from $S_2O_8^{2-}$ oxidation is 35.9%, near to 36.2%, which comes from Ag(I)/$S_2O_8^{2-}$ oxidation. It is reasonable to assume that $S_2O_8^{2-}$ can oxidize LA independently.

Table 4. Effect of Oxidants on LA Decarboxylation

Oxidants	MEK Yield/%	LA Conversion/%
Ag(I)[a]/ $S_2O_8^{2-}$	35.2	67.2
Co(II)[b]/ $S_2O_8^{2-}$	6.63	20.73
Cu(I)[c]/ $S_2O_8^{2-}$	0	25.42
Fe(II)[d]/ $S_2O_8^{2-}$	1.1	92.6
Mn(II)[e]/ $S_2O_8^{2-}$	5.91	77.42

[a] $AgNO_3$. [b] $Co(NO_3)_2$. [c] CuCl. [d] $FeCl_2$. [e] $MnCl_2$

Moreover, to our surprise, instead of MEK, MVK formed (about 10% by HS-GC) when LA reacted with Cu(I)/$S_2O_8^{2-}$. Selective oxidation of arylacetic acids in the presence of Cu(II)/ $S_2O_8^{2-}$ reaction system has been reported (Giordano et al. 1981), and the corresponding benzylacetates can be generated, and according to HS-GC-MS analysis, we conjectured that the production of MVK was associated with the further oxidation of alkyl radicals ($CH_3COCH_2CH_2\bullet$) by Cu(II) (Eq. 9) under the hydrogen-donating solution system.

$$\mathrm{Cu(I)} + \mathrm{S_2O_8^{2-}} \longrightarrow \mathrm{Cu(II)} + \mathrm{SO_4^{-}\bullet} + \mathrm{SO_4^{2-}} \tag{6}$$

$$\mathrm{CH_3COCH_2CH_2COO^{-}} + \mathrm{SO_4^{-}\bullet} \longrightarrow \mathrm{CH_3COCH_2CH_2COO\bullet} + \mathrm{SO_4^{2-}} \tag{7}$$

$$\mathrm{CH_3COCH_2CH_2COO\bullet} \longrightarrow \mathrm{CH_3COCH_2CH_2\bullet} + \mathrm{CO_2} \tag{8}$$

$$\mathrm{CH_3COCH_2CH_2\bullet} + \mathrm{Cu(II)} \longrightarrow \mathrm{CH_3COCHCH_2} + \mathrm{H^+} + \mathrm{Cu(I)} \tag{9}$$

CONCLUSIONS

In summary, efficient conversion of levulinic acid to attain high-value chemicals such as γ-valerolactone, methyl-ethyl-ketone, and methyl-vinyl-ketone was realized in this study.

Under the following conditions: 130 °C of the temperature, 1.2 Mpa of hydrogen pressure, 160 min of reaction time with the dosage of 5% Ru/C catalyst (based on the mass fraction of LA) and absolute methanol as solvent, LA conversion and GVL selectivity reached 92.90% and 99.03%, respectively.

Two new methods were developed for LA decarboxylation. CuO was found to effectively oxidize LA decarboxylation, and the molar MEK yield can reach about 67%, but the reaction conditions were relatively extreme (at 300°C for 2h). CuO/CeO_2 and $CuO/\ Al_2O_3$ could oxidize LA at lower temperature (175°C), but the product was changed to MVK. When LA was oxidized by $Ag(I)/S_2O_8^{2-}$, the reaction conditions were milder (at 160°C for 0.5h); however, the molar MEK yield was only 44.2% and Ag(I) is more expensive.

ACKNOWLEDGEMENTS

The authors are grateful to the financial support from Natural Science Foundation of China (50776035, U0733001), Foundation of Scientific Research for Universities (20070561038) from Ministry of Education of China, National High Technology Project (863 project) (2007AA05Z408), National Key R&D Program (2007BAD34B01) and National Key Basic Research Program (2010CB732201) from the Ministry of Science and Technology of China.

REFERENCES CITED

Anderson, J. M., and Kochi, J. K. (1970). "Silver(I)-catalyzed oxidative decarboxylation of acids by peroxydisulfate. The role of silver(II),"*Journal of the American Chemical Society* 92, 1651-1656.

Aschmann, S. M., Arey, J., and Atkinson, R. (1996). "OH radical formation from the gas-phase reactions of O_3 with methacrolein and methyl vinyl ketone," *Atmospheric Environment* 30(17), 2939-2943.

Braca, G., Raspoli-Galletti, A. M., and Sbrana, G. (1991). "Anionic ruthenium iodorcarbonyl complexes as selective dehydroxylation catalysts in aqueous solution," *Journal of Organometallic Chemistry* 417, 47-49.

Broadbent, H. S., Campbell, G. C., Bartley, W. J., and Johnson, J. H. (1959)."Rhenium and its compounds as hydrogenation catalysts. III. Rhenium heptoxide,"*Journal of Organic Chemistry* 24(12), 1847-1854.

Cha, J. Y., and Hanna, M. A. (2002). "Levulinic acid production based on extrusion and pressurized batch reaction," *Industrial Crops and Products* 16, 109-118.

Chang, C., Cen, P. L., and Ma, X. J.(2007). "Levulinic acid production from wheat straw," *Bioresource Technology* 98, 1448-1453.

Christian, Jr., R. V., Brown, H. D., and Hixon, R. M. (1947). "Derivatives of γ-valerolactone, 1,4-pentanediol and 1,4-di-(β- cyanoethoxy)-pentane," *Journal of the American Chemical Society* 69(8), 1961-1963.

Chum, H. L., and Ratcliff, M. (1983). "Photoelectrochemistry of levulinicacid on undopedplatinized n-TiO_2, powders," *Journal of Physical Chemistry* 87, 3089-3093.

Eberhardt, M. K. (1981)."Reaction of benzene radical cation with water. Evidence for the reversibility of OH radical addition to benzene," *Journal of the American Chemical Society* 103, 3876-3878.

Fang, Q., and Hanna, M. A. (2002)."Experimental studies for levulinic acid production from whole kernel grain sorghum," *Bioresource Technology* 81, 187-192.

Farhadi, S., Zaringhadam, P., and Sahamieh, R. Z. (2006). "Photolyticdecarboxylation of α-arylcarboxylicacidsmediated by HgF2 under a dioxygenatmosphere," *Tetrahedron Letters* 47, 1965-1968.

Gao, F., Li, R.J., and Garland, M.(2007). "An on-line FTIR study of the liquid-phase hydrogenation of 2-butanone over Pt/Al_2O_3 in d8-toluene – The importance of anhydrous conditions,"*Journalof MolecularCatalysis A: Chemical* 272, 241-248.

Gao, J., Ma, G. N., Li, Q. J., and Shi, M. (2006). "Aza-Morita–Baylis–Hillman reaction of ethyl (arylimino)acetate with methyl vinyl ketone and ethyl vinyl ketone," *Tetrahedron Letters* 47, 7685-7688.

Giordano, C., Belli, A., Citterio, A., and Minisci, F. (1981)."Electron-transfer processes: Oxidation of arylaceticacids by peroxydisulfate in acetic acid,"*Journal of the Chemical Society of Perkin I*, 1574-1576.

Guitton, J., Tinardon, F., Lamrini, R., Lacan, P., Desage, M., and Francina, A. F. (1998). "Decarboxylation of [1-^{13}C]Leucine by hydroxyl radicals," *Free Radical Biology and Medicine* 25, 340-345.

Iannone, R.,Koppmann,R., and Rudolph,J. (2009)."^{12}C/^{13}C kinetic isotope effects of the gas-phase reactions of isoprene, methacrolein, and methyl vinyl ketone with OH radicals,"*Atmospheric Environment* 43, 3103-3110.

He, Z. S. (1999). "Extraction of levulinic acid from paper- making black liquor," *Chemical Industry and Engineering* 2, 163-166.

Hoa, N. D., An, S.Y., Dung, N. Q., Quy, N. V., and Kim, D. J.(2010). "Synthesis of p-type semiconducting cupric oxide thin films and their applicationto hydrogen detection," *Sensors and Actuators B* 146, 239-244.

Hon, D. N.-S. (1994). "Cellulose: A random walk along its historical path," *Cellulose* 1(1), 1-25.

Jonsson, L., and Wistrand, L. G. (1979). "Acyloxylation of methylbenzenes by potassium peroxydisulphate," *Journalof the Chemical Society of Perkin I*, 669-672.

Joo, F., Somsak, L., and Beck, M. T. (1984). "Peculiar kinetics of hydrogenations catalyzed by chlorotris- (sulphonatedtriphenylphosphine) rhodium(I) in aqueous solutions,"*Journal of Molecular Catalysis* 24, 71-75.

Lamrini, R., Lacan, P., Francina, A., Guilluy, R., Desage, M., Michon, J., Becchi, M., and Brazier, J. L. (1998). "Oxidative decarboxylation of benzoic acid by peroxyl radicals," *Free Radical Biology Medicine* 24, 280-289.

Lou, Z. Y., Chen, X., Qiao, Y., Li, T. M., Fan, K. N.,Hea, H. Y., Zhang, X. X., and Zong, B. N. (2010). "Preparation and characterization of the chirally modified rapidly quenched skeletal Ni catalyst for enantioselective hydrogenation of butanone to R-(−)-2-butanol," *Journal of Molecular Catalysis A: Chemical*, doi:10.1016 /j.molcata. 2010.04.018.

Luo, M. F., Fang, P., He, M., and Xie, Y. L. (2005). "In situ XRD, Raman, and TPR studies of CuO/Al_2O_3 catalysts for CO oxidation," *Journal of Molecular Catalysis A: Chemical* 239, 243-248.

Luo, M. F.,Zhong, Y. J., Yuan, X. X., and Zheng, X. M. (1997). "TPR and TPD studies of CuO/CeO_2 catalysts for low temperature CO oxidation," *Applied Catalysis A: General* 162, 121-131.

Marchionni, G., Petricci, S., Spataro, G., and Pezzin, G. (2003). "A study of the thermal decarboxylation of threeperfluoropolyether salts," *Journal of Fluorine Chemistry*124, 123-130.

Martins, C. P. B.,Awan, M. A., Freeman, S., Herraiz, T., Alder, J. F., and Brandt, S. D. (2008)."Fingerprint analysis of thermolytic decarboxylation of tryptophan to tryptaminecatalyzed by natural oils," *Journal of Chromatography A* 1210, 115-120.

Mathe, F., Castanet, Y., Mortreux, A., and Petit, F. (1991). "Synthesis of 2-butanone from ethylene and methyl formatecatalysed by rhodium-iodide complexes," *Tetrahedron Letters* 32, 3989-3992.

Miller, J. D. (1968). "The kinetics of formation of a silver(II) and a silver(III) complex by peroxydislphate oxidation," *Journal of Chemical Society A 8*, 1778-1780.

Mirkhani, V., Tangestaninejad, S., Moghadam, M., and Karimian, Z. (2003). "Efficient oxidative decarboxylation of carboxylic acids with sodium periodate catalysed by supported manganese(Ш) porphyrin,"*Bioorganic and Medicinal Letters* 13, 3433-3435.

Mirkhani, V., Tangestaninejad, S., Moghadam, M., and Moghbel, M. (2004). "Rapid and efficient oxidative decarboxylation o carboxylic acid with sodium periodate catalyzed by manganese (III) Schiff base complexes," *Bioorganic Medicinal Chemistry* 12, 903-906.

O'Neill, P., Steenken, S., and Schulte-Frohlinde, D. (1975)."Formation of radical cations of methoxylated benzene by reaction with OH radicals Ti^{2+}, Ag^{2+}, and $SO4\bullet^-$ in aqueous solution. An optional and conductiometricpulse radiolysis and in situ radiolysis electron spin resonance study," *Journal of Physical Chemistry* 79, 2773-2779.

Osakada, K.,Ikariya, T., and Yoshikawa, S. (1982)."Preparation and properties of hydride triphenyl-phosphine ruthenium complexes with 3-formyl (or acyl) propionate [PuH (ocochrchrcor')(PPh_3)$_3$] (R---H, CH_3, C_2H_5; R---H, CH_3, C_6H_5) and with 2-formyl (or acyl) benzoate [RuH (o-OCCOC$_6$H$_4$COR')(PPh_3)$_3$] (R'---H, CH_3)," *Journal of Organometallic Chemistry* 231, 79-90.

Qureshi, N., Saha, B. C.,and Cotta, M. A.(2008). "Butanol production from wheat straw by simultaneous saccharification and fermentation using *Clostridium beijerinckii*: Part II—Fed-batch fermentation,"*Biomass and Bioenergy* 32, 176-183.

Schuette, H. A., and Thomas, R. W. (1930). "Normal valerolactone.III. Its preparation by the catalytic reduction of levulinic acid with hydrogen in the presence of platinum oxide," *Journal of the American Chemical Society* 52(7), 3010-3012.

Trahanovsky, W. S., Cramer, J., and Brixius, D. W. (1974). "Oxidation of organic compounds with cerium(IV). XVIII. Oxidative decarboxylation of substituted phenylacetic acids,"*Journal of the American Chemical Society* 96(4), 1077-1081.

Trapp, D., Cooke, K. M., Fischer, H., Bonsang, B., Zitzelsberger, R. U., Seuwen, R., Schiller, C., Zenker, T., Parchatka, U., Nunes,T. V., Pio, C. A., Lewis, A. C., Sealins, P. W., and Pilling, M. J. (2001). "Isoprene and its degradation products methyl vinyl ketone, methacrolein and formaldehyde in a eucalyptus forest during the FIELDVOC'94 campaign in Portugal," *Chemosphere-Global Change Science* 3, 295-307.

Walling, C., Camaioni, D. M., and Kim, S. S. (1978). "Aromatic hydroxylation by peroxydisulfate," *Journal of the American Chemical Society* 100, 4814-4818.

Williamd, D. E., and George, B. L. (1955)."Peroxytrifluoroaceticacid. V. The oxidation of ketones to esters," *Journal of the American Chemical Society* 77, 2287-2288.

Zhang, G., Shen, K. H., Zhao, D. F., Yuan, Y. K., and Wang, G. Y. (2008). "Preparation of uncoated iron oxide nanoparticles by thermal decarboxylation of iron hydroxide cetylsulfonyl acetate in solution," *Materials Letters* 62, 219-221.

Article submitted: November 16, 2010; Peer review completed: December 26, 2010; Revised version received and accepted: January 13, 2011; Published: January 15, 2011.