

Notes

Vapour phase hydrogenation of aqueous levulinic acid to γ -valerolactone over CuZnAlO hydrotalcite

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Received 29 October 2015; revised and accepted 22 April 2016

Vapour phase hydrogenation of levulinic acid to γ -valerolactone has been accomplished in aqueous phase over copper-zinc-aluminum hydrotalcite, prepared by co-precipitation method using nitrate salts as their precursors. The hydrotalcite system exhibits superior activity in the hydrogenation and cyclization of 10% aqueous solution of levulinic acid with >99% selectivity for γ -valerolactone at 275 °C under atmospheric pressure of hydrogen (flow rate of H₂-30 mL/min).

Keywords: Hydrogenation, Vapour phase hydrogenation, Hydrotalcites, Levulinic acid, γ -Valerolactone

The limited availability of fossil fuel resources, the source of petroleum products has mobilized the search for alternative renewable sources, leading to emerging a sustainable and low cost source¹⁻⁴. Biomass and its derivatives can produce carbon based intermediates, chemicals and synthetic fuels^{5,6}. γ -Valerolactone (GVL) is a potential candidate for the production of liquid alkanes used in transport, jet fuels, or as a gasoline blend. In industries, it is used as solvent for lacquers, insecticides and adhesives and some use in cutting oil, brake fluid and as a coupling agent in dye bath⁷⁻¹¹. As it is a source of sustainable energy, its synthesis has gained importance and high yields can be achieved by the hydrogenation of levulinic acid (LA). Among the variety of chemicals derived from biomass, LA forms the raw material for the production GVL as it is cheap and it can be easily produced by acid hydrolysis of carbohydrates. For the hydrogenation of LA, many homogeneous and heterogeneous catalysts based on transition metals like Ru, Pd, Pt, Ni, Cu etc., have been developed for batch reactor¹²⁻³⁰. Although many catalysts showed good selectivity for GVL, they required either harsh reaction conditions, or high H₂ pressures or temperatures, or co-catalysts or ligands, or require organic solvents unlike green solvent-like water. It is

still a challenge to develop cost effective synthetic methods for the production of GVL.

Vapour phase reaction is a continuous process for the production of interesting targets in industry, where the catalyst can be easily separated from the products and the unreacted reactants. Further, the catalyst can be easily regenerated. The hydrogenation of LA at low pressure vapour phase reaction have been reported, recently, Pravin *et al.*³¹ reported 5 wt% Ru/C gave 100% conversion of 10 wt% of LA in dioxane with 98.6% selectivity for GVL at atmospheric pressure on fixed bed down flow reactor. They also examined Cu/SiO₂ as a catalyst and obtained 100% conversion and 99.9% selectivity at 10 bar hydrogen pressure³². Chary and co-workers³³ used Cu/Al₂O₃ in the vapour phase hydrogenation of LA in water and reported 98% conversion and 87% selectivity for GVL with 0.1690 h⁻¹ WHSV (weight hour space velocity). Rao and his group³⁴ demonstrated that Ni-ZHSM-5 catalyst gives 100% conversion of LA with 92.2% selectivity for GVL. They also reported that Ni on silica gives 100% LA conversion while the selectivity for GVL is 87% (ref. 35). Venugopal and his group³⁶ identified Ru on hydroxyapatite as a good catalyst in the conversion of LA under ambient pressure of hydrogen. In spite of high activity, some of these catalysts involve high pressures and formation of byproducts. The development of catalyst for selective synthesis of GVL using molecular hydrogen is still a goal. Herein, we report our work on vapour phase hydrogenation and cyclization of 10 wt% aqueous solution of LA to GVL over CuZnAlO hydrotalcite at 1 atmospheric pressure of hydrogen with flow rate of 30 mL min⁻¹ at 275 °C.

Experimental

All the chemicals and reagents were obtained from commercial sources and were used without any further purification. Levulinic acid (LA, 98%) and γ -valerolactone (GVL, 98%), were purchased from Aldrich. Copper(II) nitrate, zinc nitrate and aluminum nitrate were purchased from SD Fine Chem Ltd.

The copper-zinc-aluminum hydrotalcite was prepared by the co-precipitation method³⁴. The mixed solution of Cu(NO₃)₂.3H₂O, Zn(NO₃)₂.6H₂O and Al(NO₃)₃.9H₂O was used as metal precursors and

1 M Na₂CO₃ solution was used as the precipitating agent. The precipitation was conducted at room temperature by simultaneous addition of metal and base solutions by maintaining the pH at ~8 to prevent the formation of CuCO₃. The precipitate was aged at 65 °C for 2 h, and then cooled to room temperature, filtered and washed with distilled water until no Na⁺ ions was detected. The precipitate was dried at 80 °C in a hot air oven for 12 h and then calcined at 450 °C in air. The calcined sample of CuZnAlO was reduced by loading in an isothermal zone of the reactor and degassed at a ramping rate of 10 °C min⁻¹ to 300 °C in nitrogen flow of 30 mL min⁻¹, which facilitates desorption of physically adsorbed water. After degassing, the sample was cooled to room temperature and the nitrogen gas was replaced by H₂ at a flow rate of 30 mL min⁻¹. Then the temperature was increased to 400 °C with a ramping rate of 10 °C min⁻¹.

The X-ray diffraction (XRD) patterns were recorded at room temperature using a Rigaku Ultima-IV diffractometer with nickel filtered Cu-K α radiation of wavelength 1.5418 Å at a power of 40 kV and a current of 20 mA in the 2 θ range of 5–80° to confirm the phases of copper present in the reduced catalysts.

The temperature-programmed reduction of hydrogen (H₂-TPR) was conducted on a Micromeritics analyzer (Auto Chem 2910) using 0.05 g of the catalyst sample. In a typical procedure, the catalyst was loaded on an isothermal zone of a quartz reactor (i.d. = 6 mm, length = 300 mm) heated by an electric furnace at a rate of 10 °C min⁻¹ to 300 °C in flowing helium gas at a rate of 30 mL min⁻¹, which facilitates desorption of the physically adsorbed water. After degassing, the sample was cooled to room temperature and the helium gas was switched to 30 mL min⁻¹ reducing gas of 5% H₂ in argon and the temperature was increased to 725 °C at a ramping rate of 10 °C min⁻¹. Hydrogen consumption was measured by analyzing effluent gas by means of thermal conductivity detector. The consumption of hydrogen was calibrated measuring the TPR of Ag₂O (50 mg), with the same protocol.

TEM was performed on a TECNAI 12 FEI TEM instrument. The samples were suspended in methanol, treated with ultrasound, and was applied to a carbon carrier foil (LaB6, KO-AP3, D = 50 μm, single tilt holder). XPS measurements were made with Kratos XPS Axis 165 spectrometer, equipped with a hemispherical energy analyzer. The non-monochromatized Mg K α X-ray source (h ν = 1253.6 eV) was operated at 5 kV and 15 mA, with pass energy of 80 eV and a

step of 0.1 eV. The samples were degassed for several hours in the XPS chamber to minimize air contamination to sample surface. In order to overcome the charging problem, charge neutralizer of 2 eV was applied and the binding energy of C 1s core level (BE = 284.6 eV) of adventitious hydrocarbon was taken as standard.

Vapor phase hydrogenation of levulinic acid was carried out in a down flow fixed bed glass reactor (11 mm i.d. and 400 mm length) at atmospheric pressure in the temperature range of 275–425 °C. In a typical experiment, 280 mg of catalyst was loaded into the reactor. Before starting the reaction, the catalyst was reduced under H₂ flow at 400 °C with a flow rate of 30 mL min⁻¹ for 180 min. After reduction, the reaction temperature was set and 10 wt% of levulinic acid in water was fed at a flow rate of 1 mL h⁻¹ (0.4 h⁻¹ WHSV) along with H₂ flow of 30 mL min⁻¹. The product mixture was collected in an ice cold trap periodically every 2 h and analyzed by GC-2010 (M/s. Shimadzu Instruments, Japan) with ZB5 capillary column, (i.d. 0.53 mm; film thickness 1.50 μm; length 30 m; initial temperature 80 °C; hold 10 min; ramp 7 °C min⁻¹ to 279 °C; hold 7 min; injection temperature 250 °C; detector temperature 280 °C (FID). The product components were identified by GC-MS. The carbon mass balance in all the measurements was >97%

Results and discussion

The XRD patterns of CZA catalyst are depicted in Fig. 1, wherein the as-prepared sample (Fig. 1a) shows the main reflections of the hydrotalcite phase³⁷. On calcination, the 2 θ reflections at 34.68°, 31.62°,

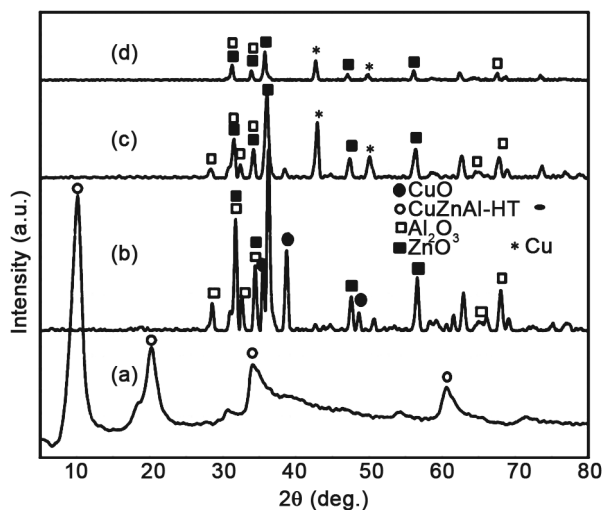


Fig. 1—XRD patterns of CuZnAlO. [(a) as prepared; (b) calcined (450 °C); (c) reduced (400 °C); (d) used sample].

32.65° and 64.9° represent the presence of Al₂O₃ (JCPDS-88-0107) (Fig. 1b), and the well resolved reflections observed at 2θ values of 38.75°, 35.55° and 48.75°, confirm the presence of CuO crystalline phase (JCPDS- 72-0629) while the reflections at 2θ values of 36.25°, 31.62°, 34.25° and 56.37°, reveal the existence of ZnO phase (JCPDS-36-1451)³⁷. The reflections due to copper or zinc aluminate were not observed. Figure 1c shows the XRD pattern of reduced catalyst, with the 2θ values at 43.2° and 50.4°, revealing the existence of metallic Cu in accordance with JCPDS-04-0836. No other copper phases (Cu(II) or Cu(I)) were detected in the XRD analysis³⁷.

The reduction behavior of the catalyst was studied by the well established temperature programmed reduction technique (TPR) with molecular hydrogen. The TPR profile of calcined CuZnAlO catalyst is shown in Fig. 2, where, a broad and single reduction peak is present in

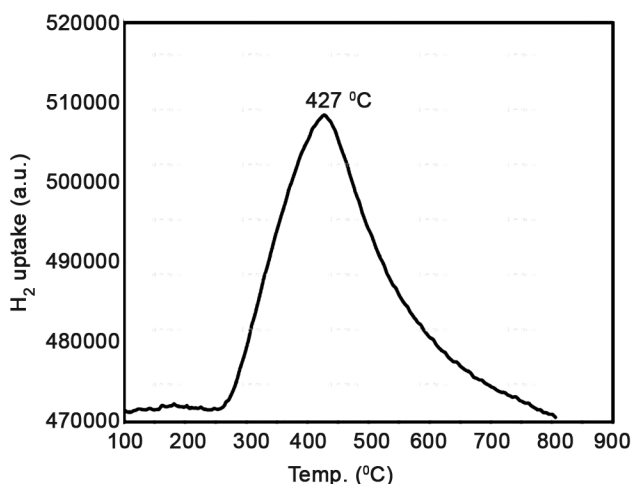


Fig. 2—TPR profile of CuZnAlO catalyst.

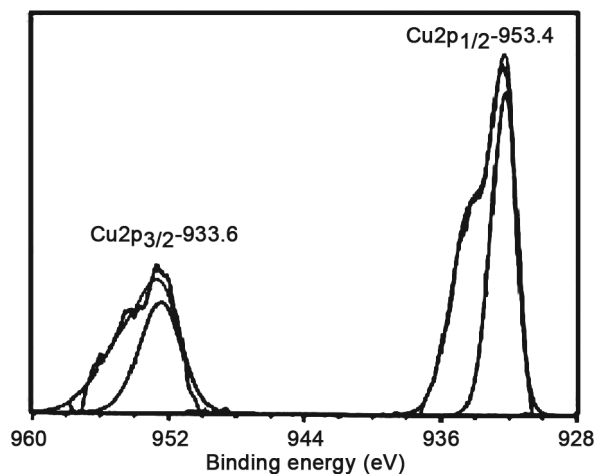


Fig. 3—XPS spectra of Cu 2p in reduced CuZnAlO.

the profile, which demonstrates that Cu(II) is directly reduced to Cu(0), and not in the sequence of CuO to Cu⁰ via Cu₂O^{38,39}. The highest reduction temperature (427 °C) of CuZnAlO sample confirms the strong interaction of Cu and support, contributing to its greater stability under reaction conditions.

X-ray photoelectron spectroscopy (XPS) is one of the important techniques to explore the oxidation state of transition metal compounds that have localized valance *d*-orbitals because of the different energies of the photoelectrons. The Cu 2*p* spectrum of the reduced catalyst is shown in Fig. 3. As evident from the Cu 2*p* spectra, there are two distinct peaks corresponding to Cu, 2*p*_{3/2} and 2*p*_{1/2} at 933.6 and 953.4 eV respectively. The Cu 2*p* peaks are either related to Cu⁰ or Cu⁺ species on the catalyst surface. Unfortunately, it is difficult to distinguish the Cu(0) and Cu(I) by XPS due to the effects of crystal size and surface coverage on the binding energy⁴⁰. The TEM image (Fig. 4a) of the reduced CuZnAlO catalyst shows porous nature. The

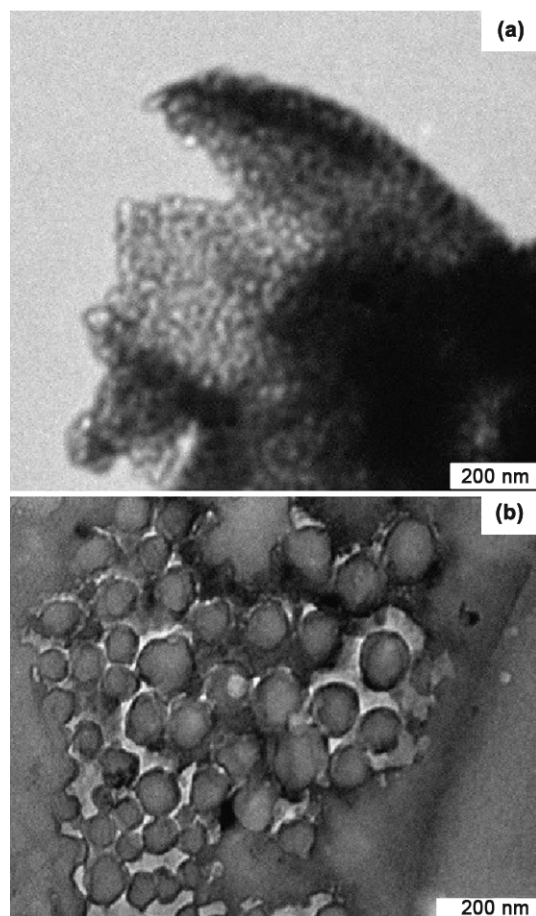
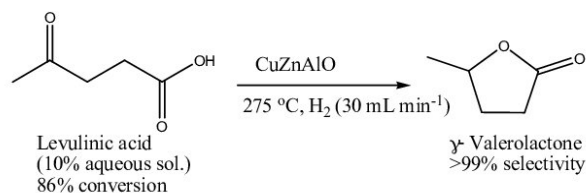


Fig. 4—TEM image of CuZnAlO (200 nm scale). [(a) reduced; (b) used catalyst].

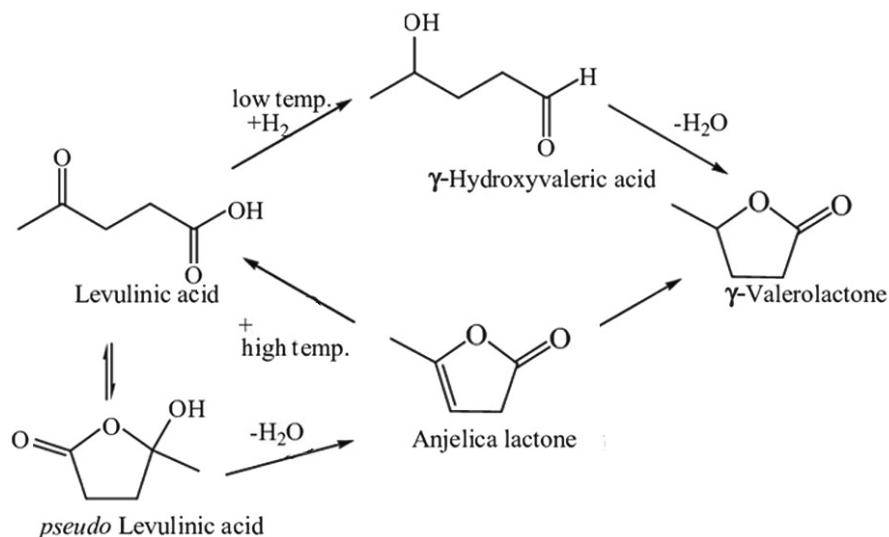
copper particle exhibited an average size between 20–40 nm.

The gas phase hydrogenation of levulinic acid over copper catalysts produced GVL as one of the main products and angelica lactone (AL) as the side product (Scheme 1). The reaction pathways are schematically represented in Scheme 2. As shown in Scheme 2, on partial reduction of levulinic acid, γ -hydroxyvaleric acid (hydrogenation) is produced, which is the key intermediate at low temperature. Subsequently, this molecule loses one water molecule (dehydration) by cyclization and forms γ -valerolactone. At higher temperatures, the pseudo-levulinic acid loses water molecule (dehydration) to form anjelica lactone (AL) (which can readily convert back to levulinic acid) which by hydrogenation forms γ -valerolactone⁴¹. Pseudo-levulinic acid coexists with levulinic acid and as the reaction proceeds, the concentration of levulinic acid decreases, indicating both the isomers have reciprocal transformation⁴².



Vapour phase hydrogenation of LA to GVL

Scheme 1



Reaction pathways for the hydrogenation of LA.

Scheme 2

To establish the optimum reaction temperature, reactions were carried out at various temperatures, viz., 275, 325, 375 and 425 °C. With increase in temperature the conversion of levulinic acid increased but the selectivity towards γ -valerolactone decreased and the formation of anjelica lactone (AL) as major product was observed (Supplementary data, Fig. S1). With this catalyst, at moderate reaction temperatures, the rate of hydrogenation of levulinic acid is higher than the rate of dehydration. Contrary to this, rate of dehydration of levulinic acid is high as large amount of anjelica lactone is observed at high temperatures. This indicates the optimum reaction temperature to be 275 °C, where the conversion of levulinic acid is 86% and the selectivity for γ -valerolactone is >99%.

To study the effect of solvent (when water is replaced by methanol) at 275 °C, the product distribution shows less selectivity for γ -valerolactone (72%) and the formation of methyl levulinate (28%) is observed by esterification of LA with methanol. This indicates there is a decrease in the hydrogenation activity of the catalyst in methanol when compared to in H_2O . Recent reports have explained the role and importance of H_2O in feed stream for the catalyst in the hydrogenation of LA to GVL^{43,44}. Venu and his group³⁶ reported 24% of ethyl levulinate formation when ethanol was used as solvent.

Indeed, high selectivity towards γ -valerolactone through hydrocyclization of levulinic acid over CuZnAlO catalyst at 1 atm pressure with a WHSV of 0.4 h⁻¹ is a noteworthy example. In order to study the

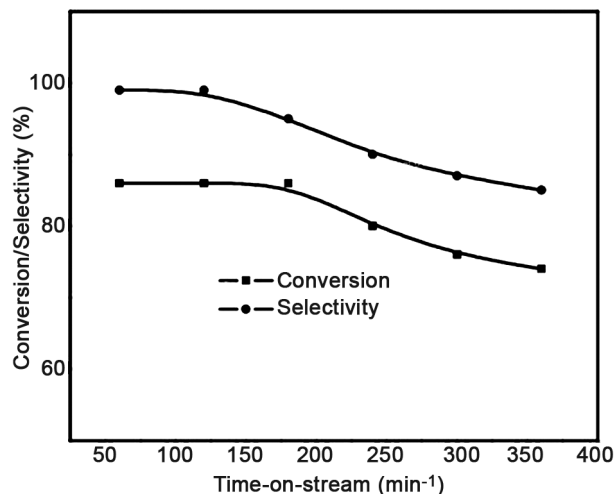


Fig. 5—Time-on-stream study over CuZnAlO catalyst for the hydrogenation of LA. [Temp.: 275 °C; WHSV: 0.4 h⁻¹; H₂ flow: 30 mL min⁻¹].

stability of the catalyst, a time-on-stream experiment was conducted at 275 °C with flow rate of 1 mL h⁻¹ (10 wt% of LA in water) WHSV of 0.4 h⁻¹ for 1440 min (Fig. 5). In the first 180 min, the conversion remained the same, while the selectivity decreased to 95% at 180 min. Beyond 180 min the LA conversion decreased from 86% to 74%. The decrease in the conversion of LA may be due to the deposition of carbon or adsorption of organic compound on the surface or when the reduced surface of metal/metal oxide upon exposure to H₂O at high temperatures converts the coordinatively unsaturated species into hydroxyl groups by dissociative adsorption on the catalyst surface⁴⁵. The XRD of the used catalyst (Fig. 1d) shows the presence of reduced copper, Al₂O₃ and ZnO phases as in the fresh catalyst, indicating that deactivation is not due to structural change but due to either carbon deposition or adsorption of organic substance on the surface of the catalyst, which is further confirmed by TEM images (Fig. 4b).

In summary, we have developed a platform technology for the hydrogenation of LA to GVL using copper catalysts at 275 °C, under hydrogen flow of 30 mL min⁻¹ with 0.4 h⁻¹ WHSV of 10% of LA in water. The CuZnAlO catalyst is a versatile, inexpensive and efficient catalyst for the hydrogenation of levulinic acid to γ -valerolactone with nearly >99% selectivity in the gas phase at 1 atm pressure.

Acknowledgement

VSJ thanks Department of Science and Technology (DST), New Delhi, India, for the award of Women Scientist Scheme (WOSA). VSJ also thanks

Dr B Sreedhar, Chief Scientist for recording TEM images and XPS.

Supplementary data

Supplementary data associated with this article, i.e., Fig. S1 is available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_55A\(05\)554-559_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_55A(05)554-559_SupplData.pdf).

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